

STUDY OF OXIDATION OF BITUMINOUS, SUB-BITUMINOUS COAL
AND LIGNITE USING ENERGY DISPERSIVE X-RAY ANALYSIS
(UP-Q7-009)

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Final Report by:

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Summary

QRL Analysis Corporation has successfully completed contract No. 23440-8-9052/01-SQ, "Study of Oxidation of Bituminous, Sub-bituminous Coal and Lignite Using Energy Dispersive X-ray Analysis (UP-Q7-009)". The following briefly outlines what has been accomplished:

The technique for analyzing oxygen to carbon ratios in coal macerals has been developed using Energy Dispersive X-Ray Microanalysis (EDXMA). Stable organic compounds were used as calibration standards. The method was used to determine the oxygen content of vitrinite samples supplied by EMR.

Methods of sample preparation suitable for both SEM and optical examination have been developed in conjunction with EMR. The methods best suited for SEM analysis are not those that have already been optimized for optical examination. Considerable difficulties were experienced in identifying the same macerals in optical samples and SEM samples. These problems have been largely resolved.

Various coal samples have been examined and analyzed. These include samples of fresh and oxidized vitrinite from western and eastern Canadian coals. Oxidized samples of eastern coals contained about 2% more oxygen than fresh samples while the increase in oxygen for western coals was about 5%. Oxygen contents determined by EDXMA were generally higher than those found by bulk analysis. This may reflect the surface analysis characteristics of EDXMA.

Oxygen distributions within macerals can now be measured and plotted in the form of oxygen concentration line scans or distribution maps. The O/C ratio or oxygen concentrations of small volumes approximating 1.5 micrometer diameter are measurable so that accurate analyses of regions of the maceral with and without minerals can be achieved. The techniques for determining local concentrations of Fe, Si, Al, S, Na, K, Ca and P were developed.

This portion of the project concentrated on vitrinite but involved other coal macerals to ensure that the procedures and results were generally applicable. In principle, the method was found to be suitable to other macerals including semi-fusinite and fusinite. The analytical method is valid for very small spatial distributions and can resolve small concentration differences, and as a result, the possibility of studying the diffusion process of oxygen into coal exists.

Based on the results of this project, it is evident that oxygen determination by EDXMA has great potential particularly in surface diffusion studies. Its practical application by the coal industry to understand problems with combustion, coking and liquifraction of oxidized coal should be developed further.

Sommaire Français

QRL Analysis Corporation ont terminé, avec succès, le contrat numéro 23440-8-9052/01-SQ, "Study of Oxidation of Bituminous, Sub-bituminous Coal and Lignite Using Energy Dispersive X-ray Analysis (UP-Q7_009)". Les points suivant profilent les accomplissements:

La technique pour analyser la proportion d'oxygène et de carbone (O/C) dans les macéraux de la houille a été développée avec la utilisation du Energy Dispersive X-ray Microanalysis (EDXMA). Des composés organique étaient employés comme référence. La méthode détermine la concentration d'oxygène dans les spécimens de vitrinite fournis par EMR.

Les spécimens sont préparés par des méthodes développées par QRL et EMR, par des méthodes appropriés pour l'examen avec un microscope d'optique ou un microscope à balayage électronique (SEM). Les méthodes qui sont appropriées pour analyser par un SEM ne sont pas nécessairement des méthodes optimum pour le microscope optique. Au commencement, on a eu des difficultés à identifier les mêmes macéraux avec le microscope optique et le SEM. Ces problèmes, pour la plupart, sont résolus.

Plusieurs spécimens de la houille étaient examinés et analysés. Ces spécimens incluent de vitrinite frais et oxydé du Canada, de l'ouest et de l'est. Les spécimens oxydés de l'est avaient 2% plus d'oxygène que les spécimens frais. Les spécimens de l'ouest avaient une augmentation de 5%. La concentration d'oxygène analyser par EDXMA était plus haute, en générale, que la concentration analysée par les méthodes globales. Cette observation est caractéristique peut-être de l'analyse de surface de la méthode de EDXMA.

La distribution d'oxygène dans les macéraux de la houille peut être mesurée et tracée dans une forme de line scan ou de cartographie distributif d'oxygène. La proportion d'oxygène et de carbone ou la concentration d'oxygène peut être analyser pour les volumes très faibles (un diamètre de 1.5 μm). Donc, les régions avec ou sans les minéraux peuvent être analyser avec précision. La technique est développée pour analyser les concentrations locales des éléments Fe, Si, Al, S, Na, K, Ca et P.

Cette partie du projet s'est concentré sur vitrinite seulement, mais les autres macéraux de la houille étaient analysés pour vérifier que la technique est applicable. En général, la technique est appropriée pour semi-fusinite et fusinite. La méthode analytique est valide pour les petites distributions spatiales et elle peut distinguer de petites différences de concentration. Par conséquent, il y a la possibilité d'étudier le processus de diffusion d'oxygène dans la houille.

Nos résultats démontrent que la détermination d'oxygène par EDXMA serait applicable à l'étude de diffusion de surface. Les applications pratiques par le industrie de la houille pour comprendre les problèmes de la houille oxydé dans les régions de combustion, de cokefaction et de liquéfaction devraient être développées en plus grand détail.

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Introduction

1.1 Background

As coal is oxidized, its chemical reactivity and calorific values are significantly altered. The environmental oxidation of bituminous coals and lignite makes combustion more difficult and poses problems to the economic development of these resources. Western Canadian coals are believed by some authorities to be comparably inert because of their high proportion of semi-fusinite content as compared to Eastern Canadian coals. This opinion is not supported by Canadian Scientists. Progress towards solving these differences requires better understanding of the oxidation processes and the resulting changes in structure. A vital step is to determine oxygen concentrations and distribution in coal macerals more accurately on a microscopic scale.

The oxygen in coal is generally divided into organic oxygen and inorganic oxygen components. Inorganic oxygen is associated with the mineral constituents of the coal while organic oxygen is chemically associated with the carbon. The direct determination of organic oxygen in coal macerals is desirable but difficult.

Surface oxidation plays a key role in modifying coal reactivity and quality. Bulk and surface organic oxygen concentrations need to be known in order to understand the mechanisms of industrial applications of coal such as combustibility, coke making, etc.

1.2 Established Methods for Oxygen Determination

The procedures used for the determination of organic oxygen in coal commonly follow the outline given in ASTM Method 3176, the Standard Method for Ultimate Analysis of Coal and Coke [1]. This method is destructive and assumes that oxygen and carbon are the only elements comprising the organic coal matrix. It is determined by difference from the results of the final analysis, based on the equation:

$$\%O_{org} = 100 - (\%C + \%H + \%N + \%S + \%ash)$$

This method is unsuitable for determining oxygen in macerals as it uses bulk analytical methods and depends on analyzing other constituents as well.

Other techniques which have been used to determine oxygen in coal directly are often classified as oxidative or reductive [2]. Oxidative methods use gaseous oxygen and reductive methods use hydrogen or reducing agents such as carbon. Fast neutron activation analysis has also been used, based on the activation of oxygen and measuring the product gamma radiation [2]. The main disadvantage of these techniques is that no differentiation is made between organic and inorganic oxygen. Therefore, the coal must be demineralized first or corrections must be made for the inorganic portion. As a result, these methods are tedious and prone to error.

1.3 Electron Beam Methods

Electron microbeam analytical methods using a scanning electron microscope with energy or wavelength dispersive x-ray microanalysis (EDXMA or WDXMA) have been successfully used in the past in the study of coal. Nandi et al. have used optical microscopy, SEM and WDXMA to study maceral matter in different coal maceral types [3]. Friel et al. have studied the distribution of sulphur in coal [4]. EDXMA is fast but until recently has not been practical as oxygen could not be measured and suitable rugged detectors were not available. The combination of the SEM and EDXMA has the potential for developing an accurate analytical method to determine oxygen in coal macerals, for identifying its microscopic distribution, and for understanding the process of coal oxidation.

Differentiation between organic and inorganic oxygen is possible either by precise location of the electron beam or by monitoring the other elements detected in the coal. The absence of significant amounts of Al, Si, Ca and Fe ensures that mineral particles are excluded when organic oxygen determination is needed. A rapid distinction of the mineral and non-mineral matter can be made visually through the SEM secondary electron image.

1.3.1 Energy Dispersive X-Ray Microanalysis

EDXMA relies on the electronic sorting of x-rays emitted from a sample. The scanning electron microscope produces a beam of high energy electrons to stimulate x-rays and as a high power microscope to locate areas for analysis. When the beam electrons impinge on the sample, they cause the emission of characteristic x-rays whose energies and intensities are directly related to the composition of the sample.

As the beam electrons enter the sample, they are scattered and spread. The

volume in which these electrons interact with the sample can be described as "onion" shaped, with a diameter of approximately 1-3 μm depending on sample density. Some x-rays generated within this volume emerge and travel in straight trajectory to a silicon lithium drifted semiconductor diode x-ray detector. The detector should be at an angle and distance to maximize the probability of collection. It is essential for accurate quantitative results that the sample surface be flat and smooth with no discontinuities such as pits or scratches. This minimizes the likelihood that the emerging x-rays will be excessively emitted, absorbed, hidden from the detector by shadowing.

EDXMA using a SEM has in the past been incapable of determining materials containing elements of lower atomic number (Z) than sodium. A thin window is required to separate the EDXMA detector which is under permanent vacuum from the SEM chamber which is at atmospheric pressure when loading samples. The conventional beryllium window used with x-ray detectors absorbs all x-rays from the light elements. However, with the advent of the ultrathin window detectors, light element detection (boron, carbon, nitrogen, oxygen and fluorine) by EDXMA is possible, and comparatively faster (few minutes) than the alternative, WDXA. Wavelength dispersive x-ray analysis can only measure one element at a time and is very slow.

1.3.2 Problems with Quantitative Light Element EDXMA

Quantitative x-ray microprobe analysis of the light elements does have various problems. The main difficulty is that the technique is new for light element analysis and there is a large uncertainty about the performance of the existing procedures used to correct for x-ray absorption and fluorescence in the material matrix. The light elements still cannot be quantitatively analyzed by direct measurement of x-ray intensity with the same confidence as elements heavier than sodium [5]. The fully quantitative analytical methods developed for EDXMA only apply to heavier elements. The lack of reliable published data on the critical correction factors makes it difficult to modify the existing software programs [6].

The large uncertainties in the mass absorption coefficients and the difficulty of sorting out the effects of contaminants are the main hurdles to using the standard corrections which are successfully applied to the heavier element analysis. These corrections, known collectively as "ZAF", involve the effects of atomic number (Z), the effects of absorption within the sample and detector (A), and x-ray induced fluorescence within the sample (F). The Z correction accounts for the effect of atomic number on excitation efficiency, fluorescent yield and detector efficiency. The A correction reflects the likelihood that, once created within the sample, an x-ray will be

absorbed before being detected. The F correction takes care of the contribution to observed peaks that arises from excitation by spurious x-rays generated within the sample.

There are specific problems associated with light element detection that are not prevalent when determining the heavy element. There is a higher tendency for their low (< 1 keV) energy x-rays to be absorbed en route to the detector window and their x-ray emissions are generally less intense. A direct result of this phenomenon is a tendency for low count rates and higher background radiation. This reduces the inherent detection sensitivity.

The methods of background modelling and subtraction presently used for the heavy element analysis are not accurate for the low energy region of the spectrum. Small errors in modelling the background before subtracting it from the peaks can make large errors in the calculated concentrations of light elements. Hence, quantitative analytical methods which rely on automatic background subtraction procedures are not valid for light element detection.

1.3.3 Light Element EDXMA using Calibration Standards.

There are simple alternatives for light element analysis to the methods where ZAF correction procedures and background subtraction are required. Excellent quantitative results can be obtained by establishing a calibration curve using the raw data from the analysis of several samples of known composition [5]. It is then a relatively simple procedure to extrapolate elemental concentrations directly from an x-ray intensity in the range of the curve. The main restriction here is that the acquisition conditions be similar if not identical for the calibration standards and the sample, and that the composition of the sample be similar to that of the standards.

A refinement of this method of analysis has been selected for the analyses of the coal samples. A calibration curve using the ratio of oxygen to carbon has greatly reduced the need for identical acquisition conditions.

The low energy region of the x-ray spectrum may contain many x-ray lines including L and M lines from the heavier elements. These lines may overlap the K line spectra of the light elements and interfere with the analysis. Examples of such overlaps are Cr, Mn, Zr and Nb in the case of carbon; Ti, Al and Zr in the case of nitrogen; Fe, Ni, V, Ti and Cr in the case of oxygen.

Considerable effort has been spent on ways to correct for these various limitations. It is essential that careful sample preparation procedures are developed. The generation of x-rays from a sample is basically from its surface and therefore it is essential that the surface be flat, smooth and free of contamination. Lower accelerating voltages decrease the probability of fluorescing from higher energy x-rays and interferences from satellite peaks are diminished. Manual background modelling techniques based on similar material matrix compositions have been shown to be more applicable to the accurate evaluation of the low energy region of the spectrum.

In the present study of coal oxidation, an accurate analytical method has been developed based on optimizing experimental parameters to eliminate or correct for the various problems discussed above. The method centres on the comparison of oxygen to carbon x-ray count ratios of samples to be determined with those of stable standard materials with known compositions. This comparison of ratios greatly reduces the sensitivity of the analysis to electron beam current fluctuations within a run and between runs.

The method has been used successfully for analysis and examination of fresh and oxidised vitrinite macerals in Western and Eastern Canadian coal samples.

Experimental Techniques

2.1 Instrumentation

2.1.1 Scanning Electron Microscopy

A JEOL model JSM-35CF Scanning Microscope was used for all scanning electron microscope examinations and microprobing procedures. The normal secondary electron mode of operation was used for most of the work supplemented by fast and normal backscattered electron detection. Accelerating voltage, which determines the electron energy, is variable between 1 kV and 39 kV. Image resolution is nominally 6 nm with about 50 nm available under conditions suitable for light element analysis. The resolution is a function of the electron beam current. Small currents (pA) provide a high resolution but noisy images and are unsuitable for microanalysis. Increasing the beam current to nanoamperes degrades resolution but produces a more contrasty image and generates more x-rays for analysis.

2.1.2 Energy Dispersive X-ray Microanalyzer

A Kevex Quantum detector attached to the SEM and a KEVEX DELTA analytical system was used for all energy dispersive x-ray microanalysis. The accompanying Kevex software was used to process the analytically acquired data. The Kevex Quantum detector contains an ultra thin window which is transparent to virtually all x-rays and so overcomes most of the previous limitations of EDXMA. A pressure differential of one atmosphere can be maintained across the window.

The analyses are usually displayed as spectra where histograms of x-ray counts are plotted as a function of x-ray energy. The peaks corresponding to specific elements are superimposed on a background or continuum of x-rays. The background is highest at low energies. The peak to background ratio is essentially insensitive to beam current but the background shape is strongly influenced by accelerating voltage. The Kevex software allows the user to select portions of the energy spectrum as "windows". The total count of x-rays in the windows are used as measures of elemental concentration. These raw data are often corrected and used for complex calculations to improve the accuracy of quantitative analyses.

Spectra are normally produced from a single spot or when scanning small area

of the sample. All material within a volume determined by the scattering of the incident electrons is analyzed. More spreading and greater penetration range occurs at high accelerating voltages.

Other display modes available are linescan and mapping where the concentration of a single element can be displayed as a function of one and two dimensional position on the sample.

2.2 Metallography

High quality analytical standards used in the vitrinite mineral matter determinations were prepared by modifications of conventional metallographic cross sectioning and polishing methods. Any polishing required at QRL was performed using the Buehler polisher and grinder. Some of the samples were prepared by EMR.

As the encapsulated samples were electrically insulating it was normally necessary to coat the specimens with thin conducting layers of either gold or carbon. Gold coatings of approximately 50nm thick were sputtered using a Technics Hummer V sputter coater. Carbon thin film coatings were evaporated onto the sample surface by carbon arc.

2.3 Preparation of Standards

2.3.1 Elemental Standards

The samples used in the development of the library of elemental standards for mineral matter determinations required by the KEVEX software were either the pure element (NBS or over 99% pure) or from high purity compounds. The list in appendix A indicates the elements collected for the library and from where they originated. It also shows the minimum detection limits for each element which will be discussed in Section 3.6.

Standard spectra were saved in software for each element at accelerating voltages of 5 and 15 kV, with their backgrounds intact. The spectra were collected for 60 seconds, at a beam current of 830 pA.

2.3.2 Carbon-oxygen standards

The carbon-oxygen standards used for developing the O/C calibration curve were carefully selected stable, high purity, high melting point compounds. These included the following:

Table 1: Carbon-Oxygen Standard Materials

<u>Compound</u>	<u>Weight Composition</u>	<u>O/C</u>
polymethylmethacrylate	60% C, 32% O, 8% H	0.53
polycarbonate	76% C, 19% O, 5% H	0.25
nylon 6/6	64% C, 14% O, 12% N	0.22
glutamic acid	41% C, 44% O, 10% N, 6% H	1.07
sucrose	42% C, 52% O, 6% H	1.24

2.3.2 X-ray Background Evaluation

The large x-ray background gave a false oxygen count when no oxygen was present. A diamond was used as a carbon standard and as a reference in the evaluation of the x-ray background at the energy of oxygen x-rays.

2.4 Coal Samples

Coal samples were provided by Energy, Mines and Resources. These included fresh and oxidized Eastern and Western Canadian coals:

Table 2: Vitrinite Coal Samples

Lingan Raw	E (carboniferous)
#26 Colly 14 North	E (carboniferous)
Devco	E (carboniferous)
Fording	W (cretaceous)
McIntyre	W (cretaceous)
White Wood	Sub-bituminous

2.5 Sample Preparation

The coal samples were prepared by following the procedures developed and specified by ASTM. At first, conventional epoxy and lucite potting were tried but this caused many complications which interfered with the SEM and EDXMA analysis. The plastics were found to charge up at a faster and more intense rate than the coal's surface. This in turn made the analysis very difficult as the incident beam became unstable. Contaminants introduced from wet polishing such as aluminum from the polishing materials affected mineral matter determinations. Ultra-sonic cleaning of the coal samples after polishing helped to eliminate this problem. As well, the water itself was found to interfere with the oxygen determinations. A vacuum desiccator was used to dry the samples.

Initially, the samples were examined optically by EMR or QRL to locate the desired areas for analysis. A scratch was made on the surface to aid in identifying and locating these particles of interest. Microhardness indentations were also made for the identification process. This procedure was employed simply to reduce analysis time.

A more detailed account of the procedures involved in the development of the method used for the analysis of the carbon-oxygen containing materials and the coal samples is provided in the discussion section. The bulk of the time spent was on this area of the study.

Results and Discussion

3.1 Optimization of Experimental Procedures

3.1.1 Effects of Atomic Number

The best technique for the determination of the heavier elements (sodium and greater), by EDXMA, is not necessarily the most appropriate for the determination of the lighter elements. Heavier elements can emit x-rays of several energies and in many instances, more than one x-ray energy is stimulated for a given accelerating voltage, giving rise to more than one emission line, enhancing its determination in the event of overlapping peaks.

As addressed in the introduction, light element detection is a more critical process than for the heavier elements. The light elements have lower energy, less intense x-rays emitted which have a tendency to not reach the detector and be absorbed by the detector window and are often masked by the heavier elemental lines.

Two sets of experimental procedures for analysis have been optimized, one based on the analyses of the heavier elements (mineral matter) and a second for carbon and oxygen determinations. Experimental parameters optimized included accelerating voltage, acquisition time, scan area and data reproducibility.

3.1.2 Effect of SEM conditions

The accelerating voltage used influences both the spatial resolution of the x-ray signal and the efficiency of the sample to excite and emit characteristic x-rays. Higher voltages produce higher energy electrons, which can penetrate deeper into the sample and spread more widely than low-energy electrons. The direct result of this is a loss of peak resolution but a more efficient excitation. At least one set of x-ray lines (K, L, or M) can be observed below 10 keV for each element. In general, it is most efficient to use an accelerating voltage that is about twice the value of the energy of the elemental line of interest. For example, the Fe K α line has an energy value of 6.4 keV R, so that an accelerating voltage of 15 kV provides ample energy to excite the iron atoms. An accelerating voltage of 15 kV was chosen as a suitable compromise for the heavier elements as each element emitted x-rays efficiently below 15 keV.

3.1.3 Effect of EDXMA Conditions

The Kevex system is most efficient when the count rate during the analysis is at least 200 counts/second. This factor served as an initial check that the analysis was preceding correctly and that SEM settings such as accelerating voltage and beam current were suitable.

3.1.4 Effect of Sample Conditions

Sample homogeneity and surface cleanliness were found to be determining factors in reproducibility during the establishment of the experimental parameters. This will be evident in the results presented below.

3.2 Experimental Optimization - Mineral Content

Preliminary analyses were performed on pure silicon dioxide and aluminum oxide as these materials have similar composition to minerals known to occur in coal. They were assumed to be chemically homogenous on a microscopic scale. They were potted in epoxy for convenience in handling, polished to a smooth flat surface and coated with a thin layer of gold. Although the oxygen determination had not being optimized at this point, it was useful to monitor the both the oxygen and the silicon or aluminum x-ray counts. The consistent ratios of oxygen counts to those of the heavier element gave some confidence that the backgrounds were not changing.

3.2.1 Analytical Reproducibility

The consistency of results obtained were examined to determine the reproducibility and precision of a particular analysis. Repeated analyses were made of the same areas on the silicon oxide sample Table 3 shows that variations of only 1.5% were observed.

Table 3: Analytical Reproducibility

<u>Time</u> (s)	<u>Area</u>	<u>Peak Area Intensity</u> (counts)	<u>Ratio</u>
60	4000X	O:7167; Si:56274	0.127
60	4000X	O:7183; Si:54630	0.131
60	4000X	O:6772; Si:53319	0.127
60	4000X	O:6819; Si:51992	0.131
100	400X	O:10692; Si:83642	0.128
100	400X	O:10302; Si:80591	0.128
100	400X	O:9940; Si:77456	0.128
100	400X	O:9707; Si:75174	0.129

3.2.2 Acquisition Time

The effect of varying acquisition time was monitored to determine the dependence of time, if any, on quantitative results. The expected linear relationship was found between acquisition time and peak area intensity (counts) for a specific area on the sample (Table 4).

Table 4: Effect of Acquisition Time

<u>Sample</u>	<u>Time</u> (s)	<u>Peak Area Intensity</u> (counts)	<u>Ratio</u>
Al ₂ O ₃	10	O:1638; Al:9957	0.165
Al ₂ O ₃	60	O:9851; Al:58619	0.167
Al ₂ O ₃	100	O:16291; Al:97577	0.167
SiO ₂	10	O:1409; Si:10787	0.131
SiO ₂	60	O:8509; Si:64269	0.132
SiO ₂	100	O:14264; Si:105122	0.136
SiO ₂	200	O:27793; Si:213703	0.130

3.2.3 Effects of Scan Area

The affect of varying scan area was monitored by changing SEM magnification and keeping all other parameters constant. Slightly larger fluctuations of up to 1.8% in the peak area intensity were observed (Table 5):

Table 5: Effect of Scan Area

<u>Sample</u>	<u>Area</u>	<u>Peak Area Intensity</u> (counts)	<u>Ratio</u>
Al ₂ O ₃	200X	O:1638; Al:9957	0.165
Al ₂ O ₃	2000X	O:1560; Al:9875	0.158
Al ₂ O ₃	20000X	O:1693; Al:10270	0.164
SiO ₂	40X	O:8509; Si:64269	0.132
SiO ₂	400X	O:8656; Si:67611	0.128
SiO ₂	4000X	O:8865; Si:68598	0.129
SiO ₂	40000X	O:8525; Si:69074	0.123

The comparatively larger fluctuations (mostly between 2 and 3% but up to 8%) here are attributed to sample inhomogeneity. Any localised impurities or variations in sample composition or surface characteristics will influence the result if the analyzed area is varied by large amounts.

These results suggest that an average of analyses of several areas on a given sample should be used to give results representative of the sample's composition.

3.2.4 Optimum Experimental Procedure - Mineral Content

From these experiments, it was concluded that for an analysis of a sample for mineral elements, the following experimental parameters provide good representative results:

Accelerating voltage:	15 kV
Acquisition time:	60-100 seconds
Scan area (magnification):	200-1000X
Areas scanned:	10
Acquisitions per area:	3

3.2.5 Simpler Experimental Procedure - Mineral Content

Under most conditions a less rigorous and quicker procedure is adequate. This was used for many of the EMR coal samples. The distribution of minerals in coal is not homogeneous and the following parameters were found to give reasonable results, representative of the vitrinite mineral matter:

Accelerating voltage:	15 kV
Acquisition time:	100 seconds
Scan area (magnification)	200-600X
Areas scanned (vitrinite):	4-10
Acquisitions per area:	1

3.2.6 Comparison with Standard Spectra

After collecting the spectra by following the experimental procedure described in Section 3.2.5, the mineral matter was quantified using the library of standards. A direct comparison was made between the spectrum obtained for a particular coal sample and spectra from the library of standards for the elements detected. Since the standard spectra and the experimental sample spectra had to be collected under different circumstances, normalization was necessary. The method used in commercial software routines employs the electron beam current as the normalizing parameter. In this study, the background x-ray spectra themselves were used as this overcame the need to keep the flux of beam electrons constant. This also overcame experimental difficulties related to backscattering, sample conductivity and charging.

This normalization was based on the comparison of a similar background count in a spectral window located away from any peaks, but close enough to obtain a representative value of the background signal. The intensities of each elemental peak in the coal spectra were compared to the intensities obtained in the corresponding standard spectra. An example of the calculation was as follows:

elemental mineral matter detected in sample: Si, Al,S

background counts from the standard: 2322

background counts from the coal sample: 5399

background normalization factor: 0.41

peak area intensity of Si standard (100%): 174708

peak area intensity of Si in coal sample: 3970

$$\% \text{ Si} = \frac{3970 \text{ counts}}{174708 \text{ counts}} \times 100\% \times 0.41 = 0.93 \text{ or } \underline{1\% \text{ Si}}$$

Detailed results for the mineral matter content of the coal samples are presented and discussed in Section 3.11 and summarized in Table 10.

3.3 Experimental Optimization - Carbon and Oxygen Determinations

3.3.1 Optimal Analytical Procedure

A different set of experimental parameters was developed for the analyses involving the determination of carbon and oxygen.

The analysis of the lighter elements is done at 5 kV because lower accelerating voltages are more efficient and interference from the heavier elements is reduced. As well, many carbon-oxygen containing materials have low melting points and are not as beam stable as metal containing materials. By lowering the accelerating voltage and keeping the acquisition time to 60 seconds sample damage was minimized and reproducibility improved.

Spot or small area analysis was chosen for those materials involved in the O/C ratio study, including the coal samples. In spot area analysis, the beam penetrates a volume approximately equal to a hemisphere of diameter 1.5 μm . This enabled analyses to be made in areas between mineral particles. This was critical in the quantification of organic oxygen in the vitrinite. By averaging the results of at least 10 areas of a particular vitrinite particle, a improved accuracy of the O/C ratio values is obtained.

Therefore, the experimental procedure used for the analysis of the carbon-oxygen

standards and for the analysis of carbon and oxygen in coal was as follows:

Accelerating voltage:	5 kV
Acquisition time:	60 seconds
Scan area:	Spot mode
Areas analyzed (vitrinite):	10

3.3.2 Reproducibility

Under repeated tests, this procedure gave consistent, results for oxygen to carbon ratios in the analysis of the known materials used in the development of the calibration curve. There was therefore confidence that the same analytical parameters would give similar results in the analyses involving the vitrinite coal samples.

3.4 Verification of Experimental Procedure

3.4.1. Standard Materials

The acquisition of suitable carbon-oxygen containing materials for the development of the calibration curve proved difficult. Many of these compounds are readily available, however few are suitable for EDXMA. Problems such as low melting points and inappropriate sample surfaces were common. It is important for accurate results that the samples analyzed have surfaces that are flat and smooth. It was equally important to find compounds that contained low amounts of oxygen since the coal samples were assumed to contain less than 20% total oxygen. Materials that were initially investigated included: diamond, potassium hydrogen phthalate, sodium oxalate, sucrose, dimethylglyoxime, glutamic acid, starch, saccharin, oxalic acid, polymethylmethacrylate, nylon 6/6 and polycarbonate. Of these compounds, only the following were usable: diamond, sucrose, glutamic acid, polycarbonate, polymethylmethacrylate and nylon 6/6. The compounds focused on were those of low oxygen content (less than 50%). The three plastic samples were very suitable. They provided low oxygen content, were beam stable and the samples obtained were flat and smooth.

3.4.2 Selection of Carbon and Oxygen Peak Windows

The carbon and oxygen $K\alpha$ lines are located at 0.282 keV and 0.523 keV respectively. The peak detected by EDXMA spans approximately 140 eV at half height with its maximum height at the keV channel of the $K\alpha$ line. If the peak areas are to be monitored for the total counts detected, windows are marked in the region of the $K\alpha$ line. The same window was consistently used for all the analyses. The carbon window spanned from 0.18-0.38 keV and the oxygen window was marked at 0.44-0.64 keV. The diamond sample served as a pure carbon standard and was the model used for evaluating the background in the region of the oxygen $K\alpha$ line. The diamond analysis resulted in an experimental O/C ratio of 0.078 as compared to a theoretical value of 0.0. The non-zero value occurs because the O/C ratios were calculated with the background intact. In the formation of the calibration curve, the value of 0.08 served as a zero point representing 0 weight % of oxygen.

3.4.3 Theoretical O/C vs Experimental O/C

The validity of the analytical parameters was confirmed by comparing experimental results to actual results expected. The carbon and oxygen peak areas were monitored for the carbon-oxygen standards. The ratio of the peak areas was plotted against the ratio of the theoretical weight percents for each standard material.

Listed in Table 6 are the results of the analyses of the known carbon-oxygen containing materials comparing experimental data to theoretical values. A linear relationship was found between experimental O/C area intensities (counts) and theoretical O/C weight percents, as depicted in Graph 1, Appendix B. This served as a confirmation that the method was behaving satisfactorily and the experimental parameters chosen were appropriate.

Table 6: Theoretical O/C vs Experimental O/C

<u>Standard Material</u>	<u>Experimental O/C</u> (ratio of cts)	<u>Theoretical O/C</u> (ratio of wt%)
diamond	0.08	0.00
nylon 6/6	0.32	0.22
polycarbonate	0.35	0.25
polymethylmethacrylate	0.51	0.53
glutamic acid	0.89	1.07
sucrose	1.22	1.24

3.4.4 Advantages of using Peak Ratios

There are definite advantages to using carbon to oxygen ratios over direct comparisons with library standards similar to the procedure discussed in Section 3.2.6. By measuring the ratio of peak areas between oxygen and carbon, it is not necessary to normalize and spectra can be acquired with different collection conditions. Spectra can be compared between the experimental sample and the standard materials in Table 6, with different beam currents, collection times, scan areas and magnifications.

The use of oxygen to carbon ratios has reduced the sensitivity to other experimental variables. These include: eliminating the need for ZAF corrections (discussed in Section 1.3.2) and adjusting for the amount of sample charging and thickness of gold coating, backscattered electron fraction and accurate background modelling. There are however a few parameters that must be kept constant: beam accelerating voltage, electronic counting parameters and peak window size.

Our method of oxygen to carbon ratios in the development of the calibration curve (Section 3.7) has simplified the procedure for organic oxygen determinations and has eliminated several experimental variables that contribute to experimental errors.

3.5 Effect of Conductive Coatings

Insulating samples frequently develop strong electrical charge in the SEM. This interferes with imaging, and analytical reproducibility becomes difficult because the beam becomes unstable. This instability causes changes in the flux of electrons entering the sample or deflects the beam onto adjacent regions of the sample.

The coal samples themselves were sometimes insufficiently conductive. Without a coating, the analyses were inconsistent because the sample surface was charging. For the cases where the coal samples were potted in epoxy, it was particularly important to provide a good electrically conductive path to the SEM ground for the coal.

The final experimental parameter of concern in the acquisition of accurate carbon and oxygen peak area intensities was therefore the affect of the thin conductive coating of sputtered gold used to prevent such charging.

Originally, a carbon coating was applied but its effectiveness in uniformly covering the sample surface was questionable. As well, the carbon arc operates at a high temperature which affected the coal surface and in some cases the epoxy as well. Gold provided better conductivity and required less heat than carbon. The optical transparency is still acceptable with the thicknesses used, which is considerably less than 50 nanometres. It however is a better electron absorber so that there is less electron penetration into the sample and it has many minor low energy x-ray peaks.

An experiment was performed on one of the carbon-oxygen containing materials to see what effect a gold coat would have on the O/C ratio. Polymethylmethacrylate was reanalysed after applying an optically transparent gold coating and the O/C ratio did not change significantly.

The gold coating greatly eased the analysis and its use was adopted for all the samples.

3.6 Minimum Detection Limits

Minimum detection limits (MDL) for all the elements involved have been calculated. MDLs are very matrix dependent and can vary considerably with instrumental operating conditions. However, MDL do provide an estimate of the accuracy of a particular elemental analysis.

The equation for calculating MDL is as follows [5]:

$$\text{MDL} = \frac{3.29 (2 \times I_b)^{1/2}}{I_n} \times C \text{ (Weight \%)}$$

where: I_b = intensity of the background (counts)
 I_n = total peak intensity (counts) - I_b
 C = concentration of the element in weight %

The values are given in Appendix A for the standard elements collected at an accelerating voltage of 15 kV and a beam current of 830 pA.

The minimum detection limits have been determined for carbon and oxygen at two accelerating voltages.

Table 7: Carbon and Oxygen MDL

<u>Element</u>	<u>MDL (%)</u>
C (15kV)	0.61
C (5kV)	0.84
O (15kV)	0.77
O (5kV)	0.96

Although the MDL was found to be less sensitive at 5 kV, it was still advantageous to operate at this low accelerating voltage. These MDL were calculated from standard spectra of diamond and sapphire whose backgrounds were simpler than the backgrounds of the coal matrix. More intense signals were observed in the region of the carbon and oxygen peak at 5 kV for the coal samples because of more efficient x-ray generation.

Based on this and on the discussion of Section 2.1 on the optimization of experimental parameters, 5 kV was the most suitable accelerating voltage for the determination of oxygen and carbon.

3.7 Development of the Oxygen Content Calibration Curve

The calibration curve constructed is a plot of theoretical weight percentages of oxygen in the carbon-oxygen compounds versus the experimental O/C ratios of the peak area intensities (counts). Listed below are the points plotted:

Table 8: Calibration Curve Data Points

<u>Sample</u>	<u>Theoretical Wt % O</u>	<u>Experimental O/C</u>
diamond	0	0.08
nylon 6/6	14	0.32
polycarbonate	19	0.35
polymethylmethacrylate	32	0.51
glutamic acid	44	0.89
sucrose	52	1.22

Graph 2, Appendix B, illustrates the curve that results from these points. The calibration curve is relatively linear over the range of oxygen concentrations. The line does however deviate from the ideal slope of 45° due in part to a process called secondary fluorescence [5]. Secondary fluorescence occurs when an x-ray is absorbed by an atom in the sample.

This atom enters into an excited state and subsequently releases the extra energy by emitting its own characteristic x-ray. Carbon is able to absorb the higher energy x-ray emitted by oxygen and consequently emits its own characteristic x-rays. This slightly lowers the signal for oxygen but in turn enhances the signal observed for carbon. This in turn lowers the value of the experimental O/C ratio which, decreases the slope of the line. Nonetheless, the linear nature of the curve provides for accurate extrapolations

for determining the oxygen content in the coal samples.

From Graph 2, Appendix B, values of weight % oxygen can be determined. A software program was used to mathematically model the best fit through the points. This model in turn was used to evaluate the weight percentages of organic oxygen in vitrinite from the experimentally acquired oxygen to carbon ratios.

3.8 Measurement of Organic Oxygen in Vitrinite Macerals

The technique to analyze oxygen content using EDXMA developed in this work was tested on coal samples from six sources. Freshly polished and oxidized samples were supplied by EMR. Only vitrinite was analyzed. Suitable macerals were identified by EMR using optical microscopy and marked with microhardness indentations. Table 9 lists the results of the analyses. For each bituminous coal, a typical fresh and an oxidized vitrinite maceral was analyzed. One sub-bituminous coal sample was also analyzed for comparison as this was expected to have a higher oxygen content. The calculated oxygen percentages were obtained using the calibration method described in section 3.7.

The fresh samples were kept at 0°C until marked and then stored at 9°C until analyzed. The oxidized coal samples had been heated in air for 48 hours at 105°C and then marked and stored at 9°C until analyzed. The time between polishing and analysis was approximately 5 days.

Table 9: Oxygen Content of Vitrinite Particles

<u>Coal Sample</u>	<u>Type</u>	<u>Exper. O/C</u>	<u>Calculated % O</u>
<u>Bituminous Coal:</u>			
<u>Eastern Canadian:</u>			
#26 Colly 14 North	Fresh	0.197	9.6 $\pm$ 0.30
#26 Colly 14 North	Oxidized	0.269	13.7 $\pm$ 0.30
Devco	Fresh	0.200	9.8 $\pm$ 0.35
Devco	Oxidized	0.327	17.0 $\pm$ 0.35
Lingan Raw	Fresh	0.207	10.2 $\pm$ 0.30
Lingan Raw	Oxidized	0.289	14.9 $\pm$ 0.45
<u>Western Canadian:</u>			
McIntyre	Fresh	0.119	5.2 $\pm$ 0.15
McIntyre	Oxidized	0.162	7.6 $\pm$ 0.20
Fording	Fresh	0.151	7.0 $\pm$ 0.25
Fording	Oxidized	0.166	7.9 $\pm$ 0.25
<u>Sub-bituminous Coal:</u>			
White Wood	-----	0.828	45.5 $\pm$ 0.5

Appendix C contains a representative spectrum collected for each of the coal samples analyzed, illustrating the carbon and oxygen peaks that were monitored.

The fresh Eastern Canadian coal samples were found to have up to twice as much oxygen as the Western Canadian coal samples and absorbed even more oxygen during oxidation. The unoxidized sub-bituminous coal sample supplied by EMR had an

unusually high amount of oxygen (45.5% compared with the expected value of 20-25%). This could be due in part to the moisture content of the sample. Samples that are not sufficiently dry would result in high oxygen values due to the detectable oxygen from the water.

3.9 Surface Electrical Conductivity

Good SEM imaging requires an electrically conducting sample to avoid problems associated with electrical charge retention which deflects or defocuses the electron beam. Significant differences in the amounts of sample charging and hence surface electrical conductivity were observed between the samples.

All the coal samples were initially coated with a similar thin layer of gold to suppress electrical charging. As the amount of surface oxygen increased, the less effective was this coating at suppressing charging effects. This was particularly evident with the sub-bituminous, White Wood sample. A second coating of gold was required in order to analyze the sample (total 2 minute coating). As the carbon content decreases, so does the electrical conductivity and as a result, charging effects become greater. #26 Colly 14 North and Lingan Raw samples required a coating for 1.5 minutes as opposed to 1 minute for the other samples due to these charging effects. This is in agreement with the increased oxygen detected (with the exception of Devco).

3.10 Relevance to Reactivity and Fluidity

Our observed results of initial organic oxygen content are in keeping with the results expected from large scale combustibility and coking experiments.

Chemical reactivity and fluidity are good for both Eastern and Western coals in the fresh state. Eastern coals are more fluid and more reactive than the Western coals. The Eastern coals contain functional groups that are highly reactive. These desirable properties are adversely affected when the coal's surface becomes oxidized. The reactive functional groups are converted to a less reactive almost inert state during oxidation and effectively seal the interior from further reaction.

The Eastern coals oxidized more than Western coals. Total organic oxygen content increased by 4.0% for #26 Colly 14 North to 7.2% for Devco. Western coals only increased by 0.9% (Fording) to 2.4% (McIntyre).

3.11 Mineral Determinations

Each of the coal samples analyzed for the O/C ratios were analyzed again for the mineral matter, using the optimized parameters established in Section 3.2.

Table 10 summarizes the results of the experiments to determine the mineral matter constituents of each of the coal samples. Included are the oxygen weight percentages as calculated in Section 3.8 and the carbon content calculated by difference. This provides an overall summary of the elemental content of the vitrinite samples as determined by EDXMA:

Table 10: Elemental Content of Vitrinite Samples

<u>Coal Sample/Type</u>		<u>Elements Detected in Weight %</u>							
		C	O	S	Ca	Fe	Si	Al	Ti
<u>Bituminous Coal:</u>									
<u>Eastern Canadian:</u>									
#26 Colly - 14 North	Fresh	83	10	5	0	0	1	1	0
	Oxid	78	14	6	0	0	1	1	0
Devco	Fresh	83	10	5	0	0	1	1	0
	Oxid	76	17	5	0	0	1	1	0
Lingan Raw	Fresh	82	10	6	0	0	1	1	0
	Oxid	77	15	6	0	0	1	1	0
<u>Western Canadian:</u>									
McIntyre	Fresh	89	5	4	0	0	1	1	0
	Oxid	85	8	4	0	0	1	1	1
Fording	Fresh	87	7	4	0	0	1	1	0
	Oxid	86	8	4	0	0	1	1	0
<u>Sub-bituminous:</u>									
White Wood	---	45	46	3	2	2	1	1	0

Appendix C contains a spectrum of each vitrinite sample representing the analysis for mineral matter determinations.

As expected the oxidation of the vitrinite samples had little or no effect on the mineral content as many of these are already oxides. In general, only sulphur, aluminum and silicon were detected as mineral matter in vitrinite. Sodium, potassium and phosphorus were not detected in the vitrinite samples (minimum detection limits of 0.11%-0.26%). Calcium and iron were only detected in the vitrinite of sub-bituminous White Wood sample (minimum detection limits of 0.21%-0.57%). Titanium was only detected in the oxidized McIntyre vitrinite sample (detection limit 0.33%).

3.12 Potential Areas of Study

During the development of the method and procedures discussed above, many other potential areas of study surfaced. These included: oxidative studies of other macerals, direct maceral identification from the secondary electron image (eliminating the initial optical examination stage), correlation of EDXMA measurements and microhardness testing and measurement of oxygen diffusion profiles. These areas would widen the practical applications for the coal industry and help understand the oxidation process.

3.12.1 Oxidation of Other Coal Macerals

We have already shown that a definite difference exists between the oxygen content of fresh and oxidized vitrinite macerals of Western and Eastern Canadian coals. This work could be extended further to other coal macerals. In our preliminary investigations, vitrinite and semi-fusinite particles of Fording coal were analyzed to compare the O/C ratios. The table below summarizes what was found:

Table 11: Maceral Oxidation

<u>Maceral</u>	<u>Exper. O/C</u>	<u>Weight % O</u>
Vitrinite	0.193	9.4 ± 0.9
Semi-Fus.(non-mineral area)	0.226	9.9 ± 1.0
Semi-Fus.(mineral area)	0.644	35.0 ± 1.8

As expected, the semi-fusinite non-mineral matter, has a higher average oxygen content than vitrinite. There are no mineral rich areas in vitrinite. One would expect a large difference between the mineral and non-mineral matter of the semi-fusinite. This detectable difference allows for the direct distinction between mineral and non-mineral matter and to some extent between vitrinite and semi-fusinite.

3.12.2 Maceral Identification

Some time has been spent on identifying the maceral particles directly from secondary electron imaging. The same Fording coal sample from Section 3.12.1 was used.

Vitrinite, semi-fusinite and fusinite were located optically, mapped and a reference photograph (Figure 1) was taken by EMR of an area where each maceral was present for comparison with SEM micrographs. The dark cross in the centre of the photograph is a scratch that was used to map the area. In the very top left hand quadrant is a semi-fusinite particle (SF). In the same quadrant, but closer to the junction of the lines is a smaller vitrinite particle (V). Directly below this vitrinite particle is a fusinite (F) maceral with the x-axis of the scratch passing through it. There is another semi-fusinite/fusinite (SF-F) particle in the top right quadrant, sitting on the x-axis of the scratch.

Figure 2 is an SEM micrograph (secondary electron image) showing the same particles after applying a thin gold coating. Each of the marked particles were

magnified to provide more detailed SEM micrographs (Figures 3 to 6). The advantage of the SEM images is that the visible contrasts are directly related to differences in atomic number. The brighter the area, the heavier the element comprising the material. Therefore, the mineral matter appears as the brighter material, while the non-mineral matter appears duller and darker.

The secondary electron imaging coupled with the EDXMA results provide the means necessary to accurately distinguish between the different macerals. There is also the possibility of using back scattered electron imaging which further enhances atomic number differences of a given area. These methods of identifying coal macerals without the need for expensive cross sectioning and polishing could reduce both the analysis time and cost per sample.

Figure 7 and 8, Appendix E are QRL optical photographs of the same Fording coal sample. Figure 7 is similar to Figure 1, no gold coating while Figure 8 is the coal sample after applying a thin gold coating. The coal macerals are still identifiable.

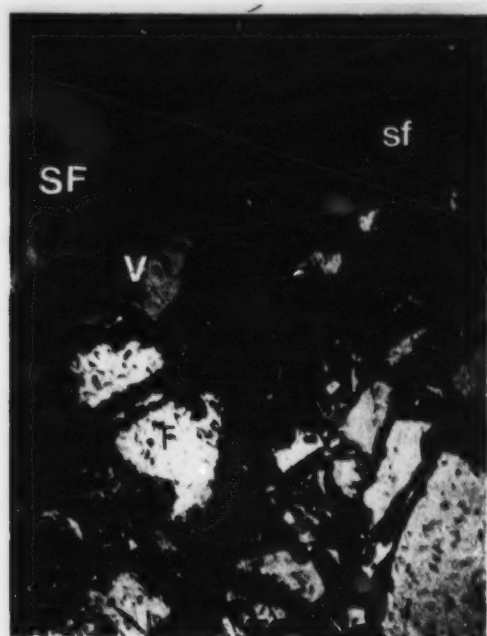


FIGURE 1 EMR Optical 100X

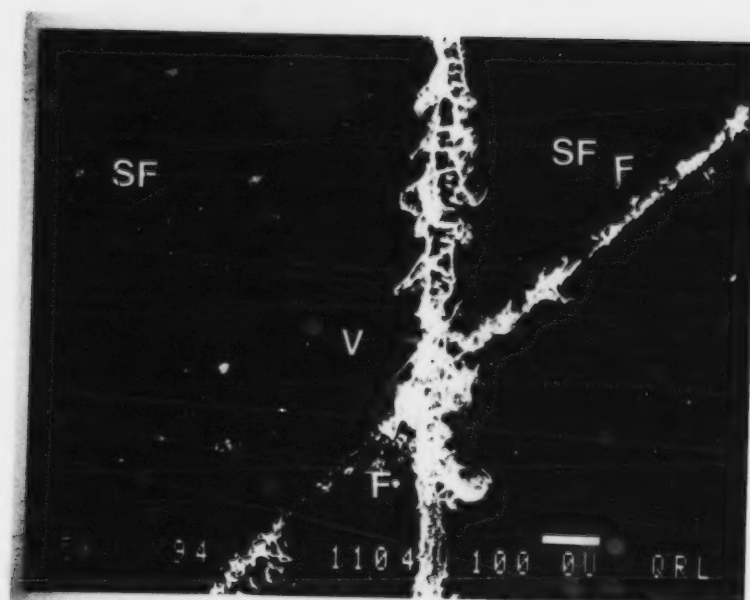


FIGURE 2 SEM 94X

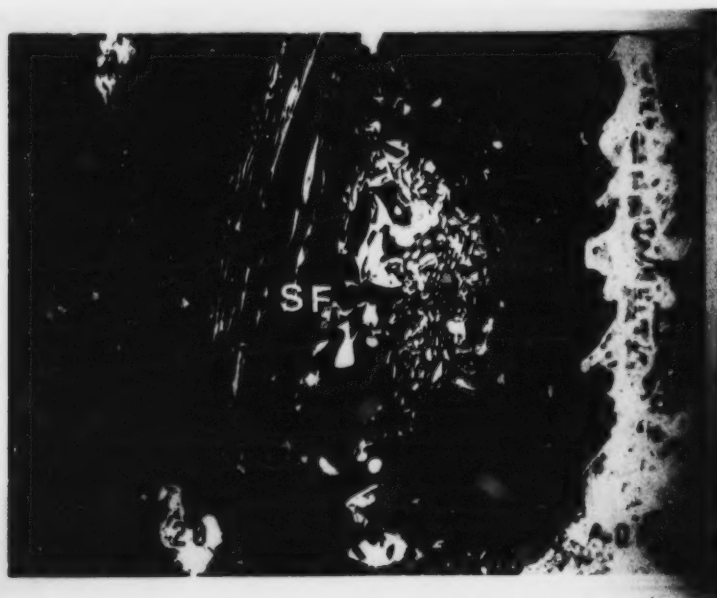


FIGURE 3 SEM 120X



FIGURE 4 SEM 480X



FIGURE 5 SEM 200X

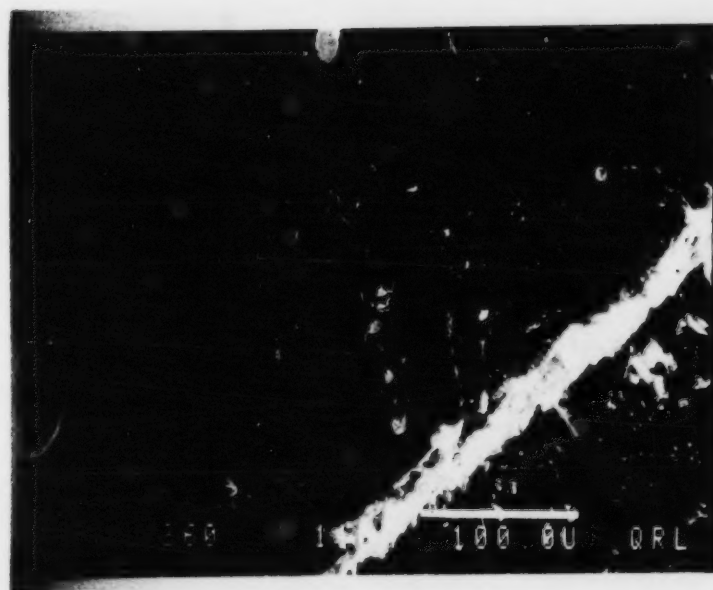


FIGURE 6 SEM 260X

3.12.3 Correlation Between EDXMA and Microhardness Testing

In this work, microhardness impressions have only been used to identify specific areas of interest. There is however the potential of correlating the microhardness testing to the results of the oxygen determinations by EDXMA. Microhardness tests have been used to monitor the oxygen penetration into coal particles [7]. Nandi et al. have shown that changes in the microhardness impressions occur as a direct result of oxidation. As oxygen reacts with the surface of the coal particle, the physical state changes. The plastic state of fresh vitrinite is transformed into an elastic state by oxidation. As a result of this, the microhardness impressions "bounce back" and the faces of the impressions return to the horizontal plane leaving two crossed lines. The size, appearance and any physical changes of the microhardness impressions are easily characterized by the SEM secondary electron image. The chemical changes, (oxygen content) could be monitored close to the indentations using the EDXMA technique developed above. We have shown that the differences in surface oxygen content between fresh and oxidized coal samples are detectable. By combining the two techniques, insight into the degree of oxidation and the changes in the physical state of the maceral can be studied.

The EDXMA technique can be developed further to be more accurate and have better resolution if oxygen concentration line scans are plotted. These are achieved by continuously measuring oxygen x-ray counts as the beam is scanned along a line from the edge of the maceral to its centre. The oxygen linescans are accurate to approximately 1%.

An illustration of oxygen linescans is given in Figures 9 and 10. Figure 9 is an oxygen linescan of two separate particles of calcite mounted in epoxy. The straight line indicates the location of the linescan and the fluctuating line is the actual scan. This line varies in height with varying oxygen concentration. This variation in line height is illustrated better in Figure 10. This shows an oxygen linescan through aluminum oxide (A) and silicon dioxide (B) mounted in epoxy. There is a definite change in height visible from scanning through epoxy, to the aluminum oxide (47% O), to the silicon dioxide (53%), an oxygen concentration difference of only 6%.

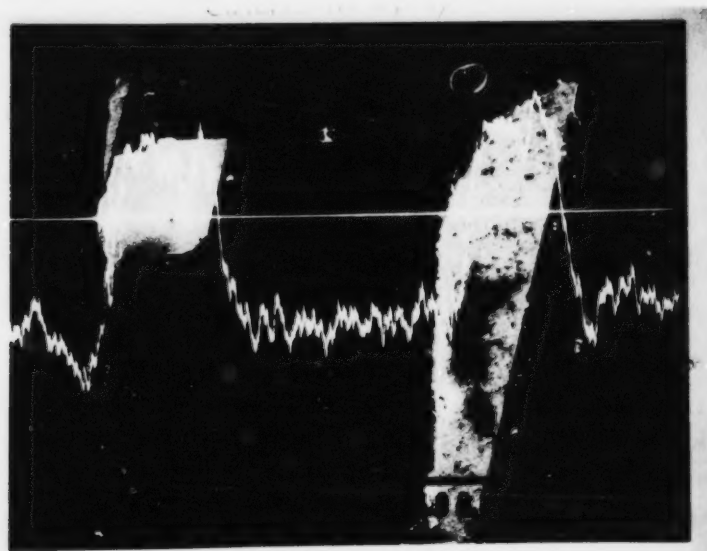


FIGURE 9 SEM Oxygen Linescan 26X



FIGURE 10 SEM Oxygen Linescan 20X

3.12.4 Diffusion Profiles

By measuring oxygen content as a function of distance from the edge of a maceral particle using the linescan method, a diffusion profile depicting the degree or depth of oxidation can be established. Diffusion profiles would also serve as a means to examine how the different coal macerals are affected by oxidation.

Diffusion profiles could also be used for studying the rate of oxidation. Comparisons could be made between profiles of fresh, environmentally oxidized and controlled laboratory oxidized coal samples. This could serve as a method of determining the extent of oxidation. Studies could be performed to determine how time and temperature affect the rate and degree of oxidation.

Conclusions

The purpose of this study was to investigate the oxidation of coal vitrinite maceral. The combination of scanning electron microscopy and energy dispersive x-ray microanalysis has proven to be well suited to the study of coal oxidation. With the advent of the ultrathin window detectors, light element detection in EDXMA is possible and very much faster than WDXA. Oxygen concentrations as low as 1% can be measured in such small areas that accurate analyses of regions with or without minerals can be routinely achieved.

QRL Analysis Corporation has developed a technique for determining oxygen in coal macerals. The method is based on a calibration curve developed from the ratio of oxygen to carbon x-ray counts of stable organic materials. Using the oxygen and carbon peak area intensity ratios rather than single peak heights eliminates most of the difficulties in controlling experimental variables of the EDXMA process. The theoretical weight percent of oxygen was plotted against the experimentally obtained O/C ratios for the organic materials. The validity of the method was verified by the linear correlation between the experimental O/C peak area intensity ratios and the theoretical O/C weight percent ratios in the range of oxygen contents from 0 to 52%.

The O/C ratios and hence oxygen content of vitrinite were measured in various fresh and oxidized Eastern and Western Canadian coal samples. The oxidized samples had been oxidized for 48 hours at a temperature of 105°C. On average, the Western Canadian coal samples were found to contain less oxygen than the Eastern Canadian coal. The Eastern Canadian coal was affected more by the oxidation process as the surface oxygen content rose to as high as 17.0% as compared to a high of 7.9% for the Western Canadian coal.

The mineral matter distributions have also been studied on the vitrinite of the coal samples. The technique for determining local concentrations of Fe, Si, Al, Ti, S, Na, K, Ca, and P were developed based on direct comparisons with standards. In general, the coal samples were found to contain Si, Al, S with only Fe and Ca being detected in the sub-bituminous coal sample. There is very little mineral matter in vitrinite and it is evenly distributed throughout the maceral.

The work has demonstrated the potential for other areas of study that would further expand the practical application of SEM and EDXMA for the coal industry by helping understand the surface oxidation process. Although this study has concentrated on the vitrinite maceral, preliminary investigations have found that the methods developed are suitable for other coal macerals including semi-fusinite and fusinite. The direct identification of the different macerals from secondary and backscattered electron

imaging would reduce both analysis time and cost per sample. The initial optical mapping stage and special polishing techniques could be reduced or eliminated.

Changes in the physical state of coal macerals during oxidation could be monitored by correlating EDXMA results to microhardness testing. The degree of oxygen penetration has a direct effect on the plasticity of fresh vitrinite. EDXMA can determine the oxygen concentrations of the vitrinite while the changes in hardness and plasticity could be monitored by SEM examination of the microhardness impressions.

The degree or depth of oxidation could be monitored by diffusion profiling. This would involve measuring the oxygen content as a function of distance from the edge of a maceral particle. Diffusion profiles would also examine how the different coal macerals are affected by oxidation.

EDXMA is a non-destructive, element selective analytical technique capable of analyzing most elements at concentrations as low as 0.5%. Our technique has extended the working range of EDXMA to give accurate quantitative results for oxygen and carbon. This extends the possibilities for other areas of light element determinations such as the analysis of plastics and organic substances.

The main problem in selling Western Canadian coal to foreign markets is the presence of unusually high percentages of semi-fusinite. According to European coal scientists, semi-fusinites are practically inert, but it appears from work of Canadian Scientists that the semi-fusinites are more than 60% reactive. Indications from our preliminary study show that there is a definite possibility that we could confirm the findings of the Canadian Scientists.

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Appendix A: Library of Standards with MDL

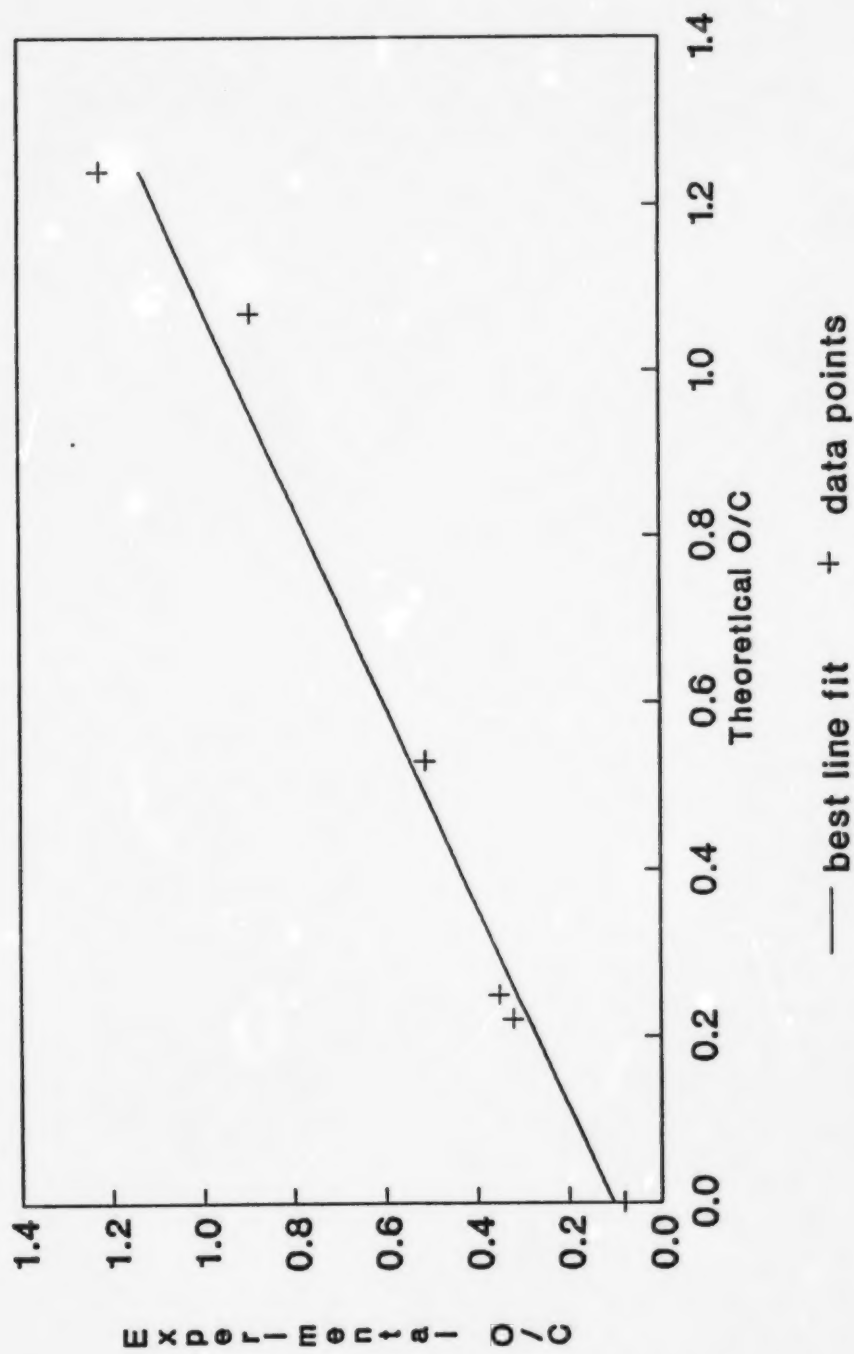
<u>Element</u>	<u>Origin</u>	<u>MDL(%)</u>
Ag	pure metal	0.53
Al	sapphire	0.25
As	gallium arsenide	0.63
Au	pure metal	0.46
B	boron nitride	1.54
C	diamond	0.61
Ca	calcite	0.21
Cd	pure metal	0.49
Cl	sodium chloride	0.23
Cr	pure metal	0.44
Cu	pure metal	0.57
F	teflon	0.40
Fe	pure metal	0.57
Ga	gallium arsenide	0.33
K	potassium hydrogen phthalate	0.11
Mg	pure metal	0.17
Mo	pure metal	0.47
N	boron nitride	0.81
Na	sodium chloride	0.26
Nb	pure metal	0.40
Ni	pure metal	0.31
O	sapphire	0.77
Pb	pure metal	0.51
S	pyrite	0.35
Si	quartz	0.21
Sn	pure metal	0.49
Ta	pure metal	0.44
Ti	pure metal	0.33
V	pure metal	0.38
W	pure metal	0.52
Y	pure metal	0.35
Zn	pure metal	0.42
Zr	pure metal	0.39

Appendix B: Graphs

Graph 1: Theoretical O/C vs Experimental O/C

Graph 2: Theoretical Weight % O vs Experimental O/C

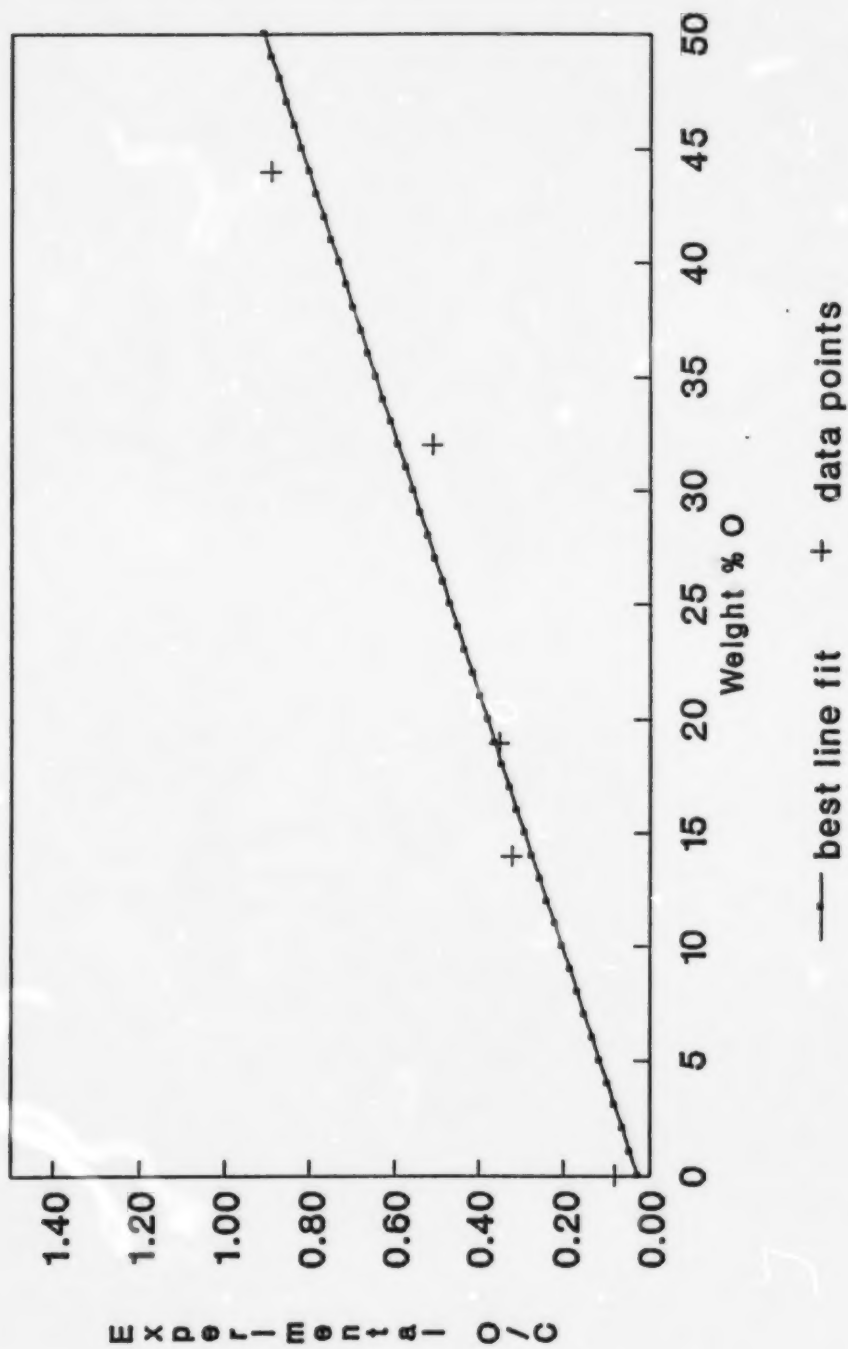
GRAPH 1
Theoretical O/C vs Experimental O/C



6 kV - Background Intact

GRAPH 2

Weight % O vs Experimental O/C



5 kV - Background Intact

Appendix C: SpectraO/C Ratio Analysis:

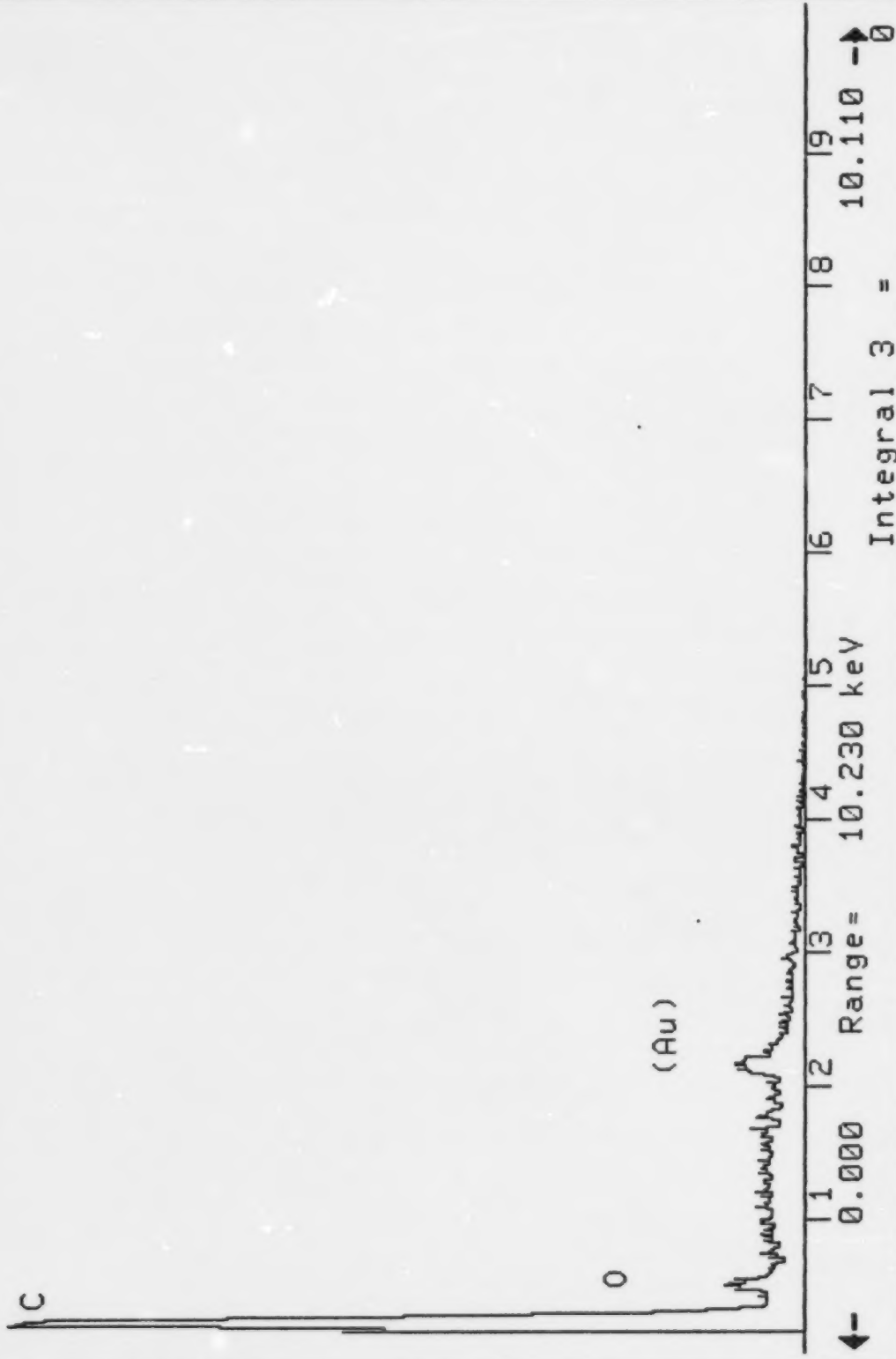
- Spectrum 1: McIntyre Fresh Coal
- Spectrum 2: McIntyre Oxidized
- Spectrum 3: Fording Fresh Coal
- Spectrum 4: Fording Oxidized
- Spectrum 5: #26 Colly 14 North Fresh
- Spectrum 6: #26 Colly 14 North Oxidized
- Spectrum 7: Devco Fresh Coal
- Spectrum 8: Devco Oxidized
- Spectrum 9: Langan Raw Fresh Coal
- Spectrum 10: Langan Raw Oxidized
- Spectrum 11: White Wood (sub-bituminous)

Mineral Analysis:

- Spectrum 12: McIntyre Fresh Coal
- Spectrum 13: McIntyre Oxidized Coal
- Spectrum 14: Fording Fresh Coal
- Spectrum 15: Fording Oxidized Coal
- Spectrum 16: #26 Colly 14 North Fresh
- Spectrum 17: #26 Colly 14 North Oxidized
- Spectrum 18: Devco Fresh Coal
- Spectrum 19: Devco Oxidized Coal
- Spectrum 20: Langan Raw Fresh Coal
- Spectrum 21: Langan Raw Oxidized
- Spectrum 22: White Wood (sub-bituminous)

6-Mar-1989 13:42:23

O/C Ratio Analysis - McIntyre Fresh Coal Preset= 60 secs
Vert= 1143 counts Disp= 1 Elapsed= 60 secs

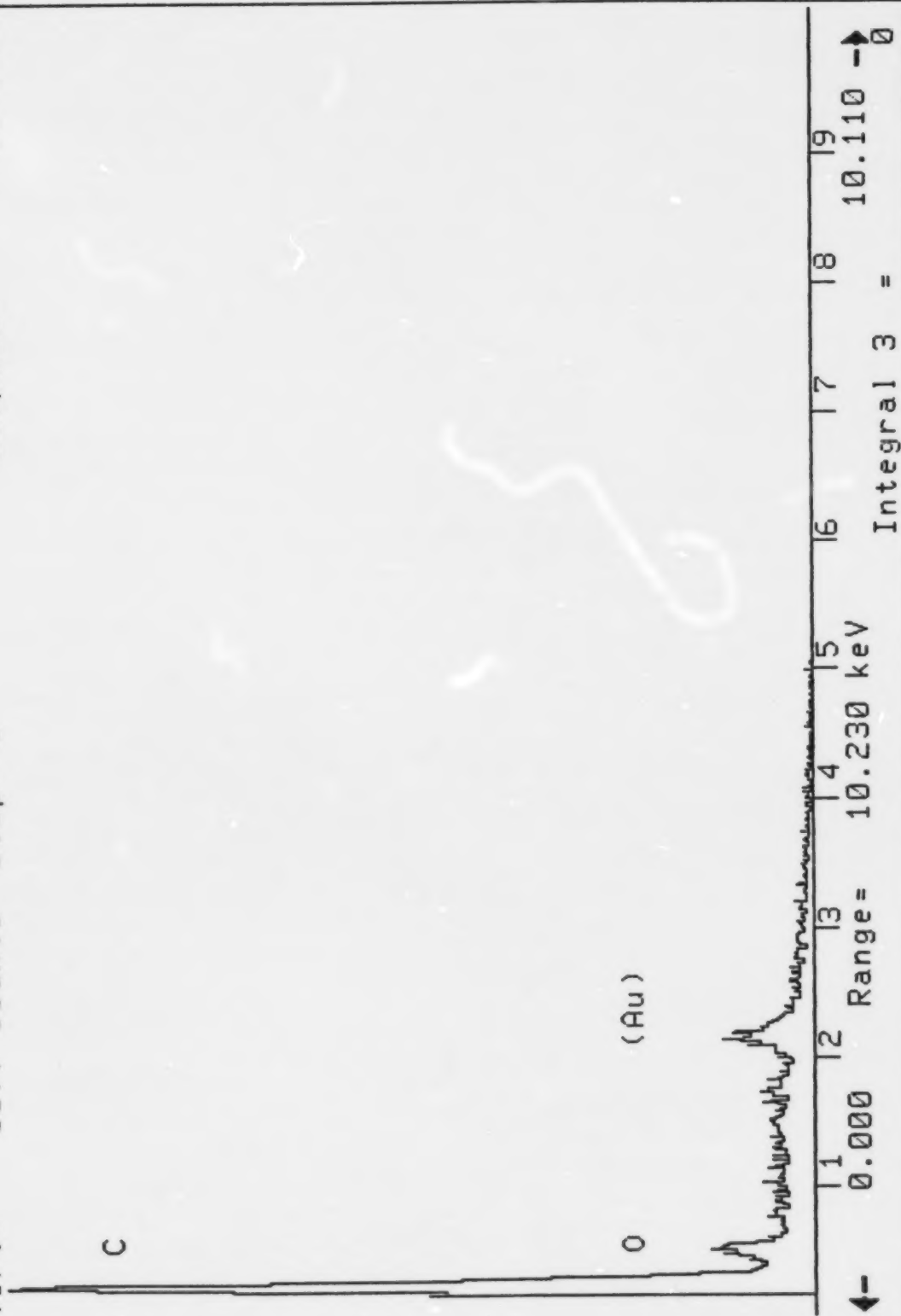


6-Mar-1989 13:39:07

O/C Ratio Analysis - McIntyre Oxidized
Vert= 1177 counts Disp= 1

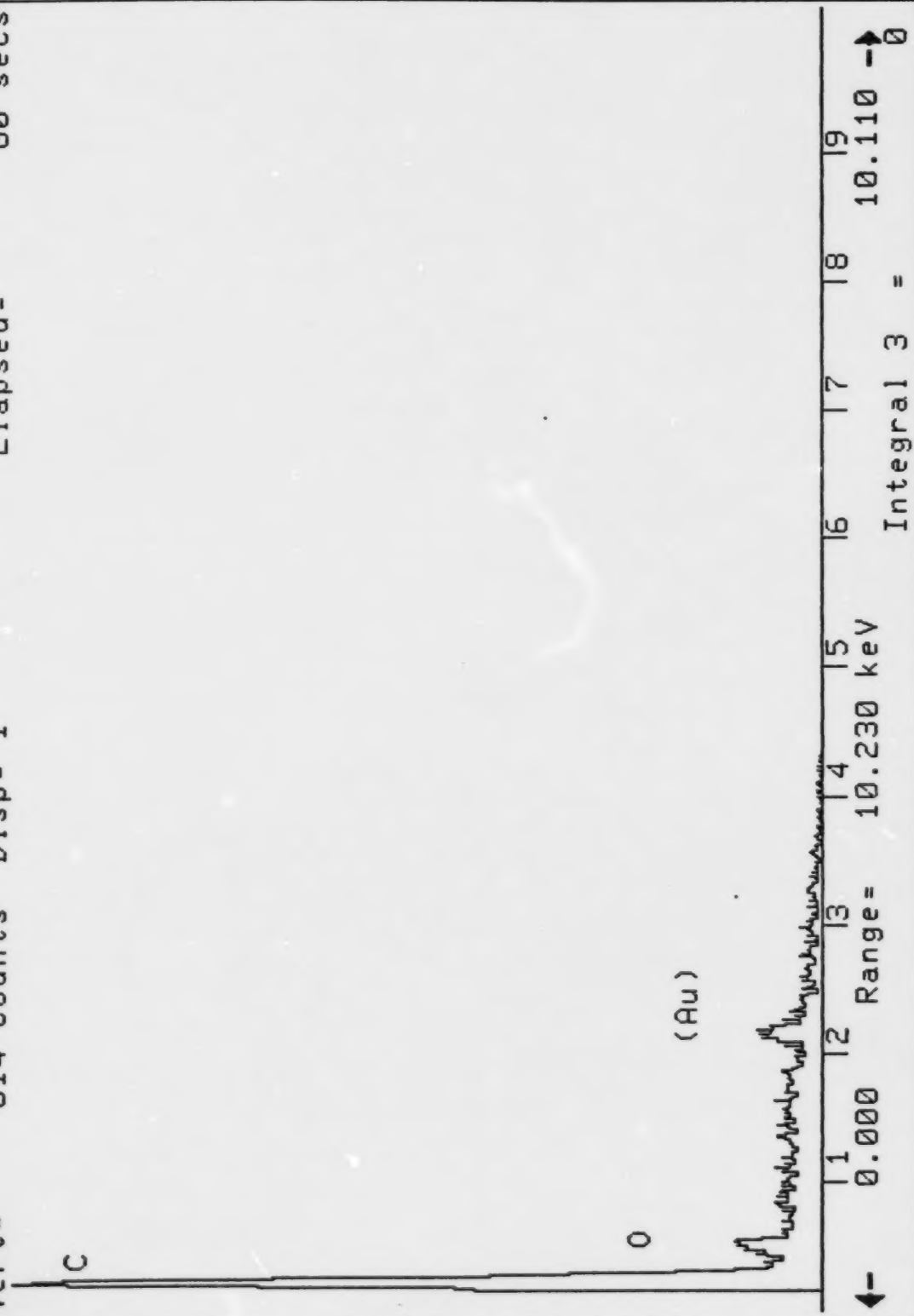
Preset=
Elapsed=

60 secs
60 secs



6-Mar-1989 13:47:39

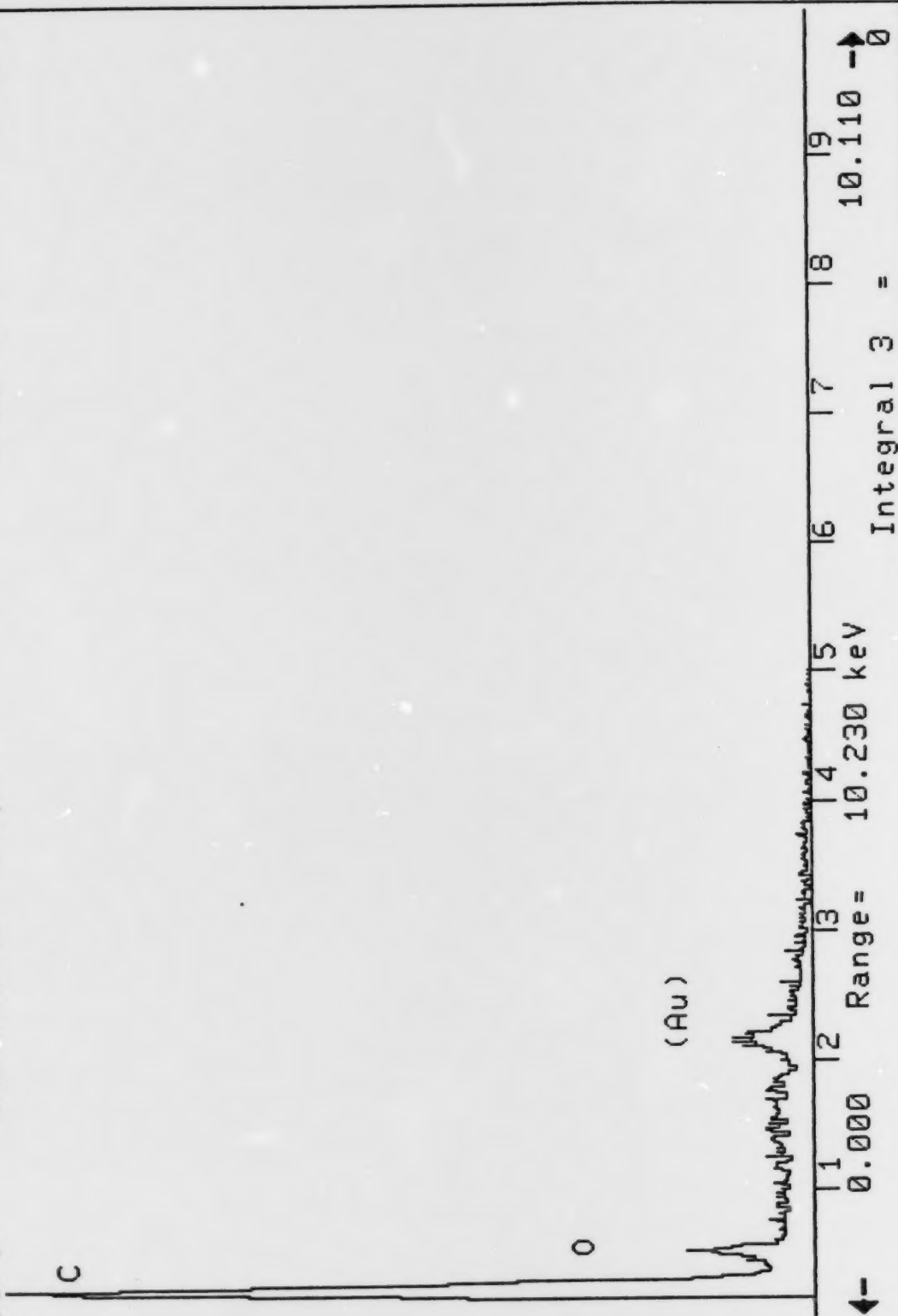
O/C Ratio Analysis - Fording Fresh Coal Preset= 60 secs
Vert= 814 counts Disp= 1 Elapsed= 60 secs



6-Mar-1989 13:50:08

O/C Ratio Analysis - Fording Oxidized
Vert= 823 counts Disp= 1

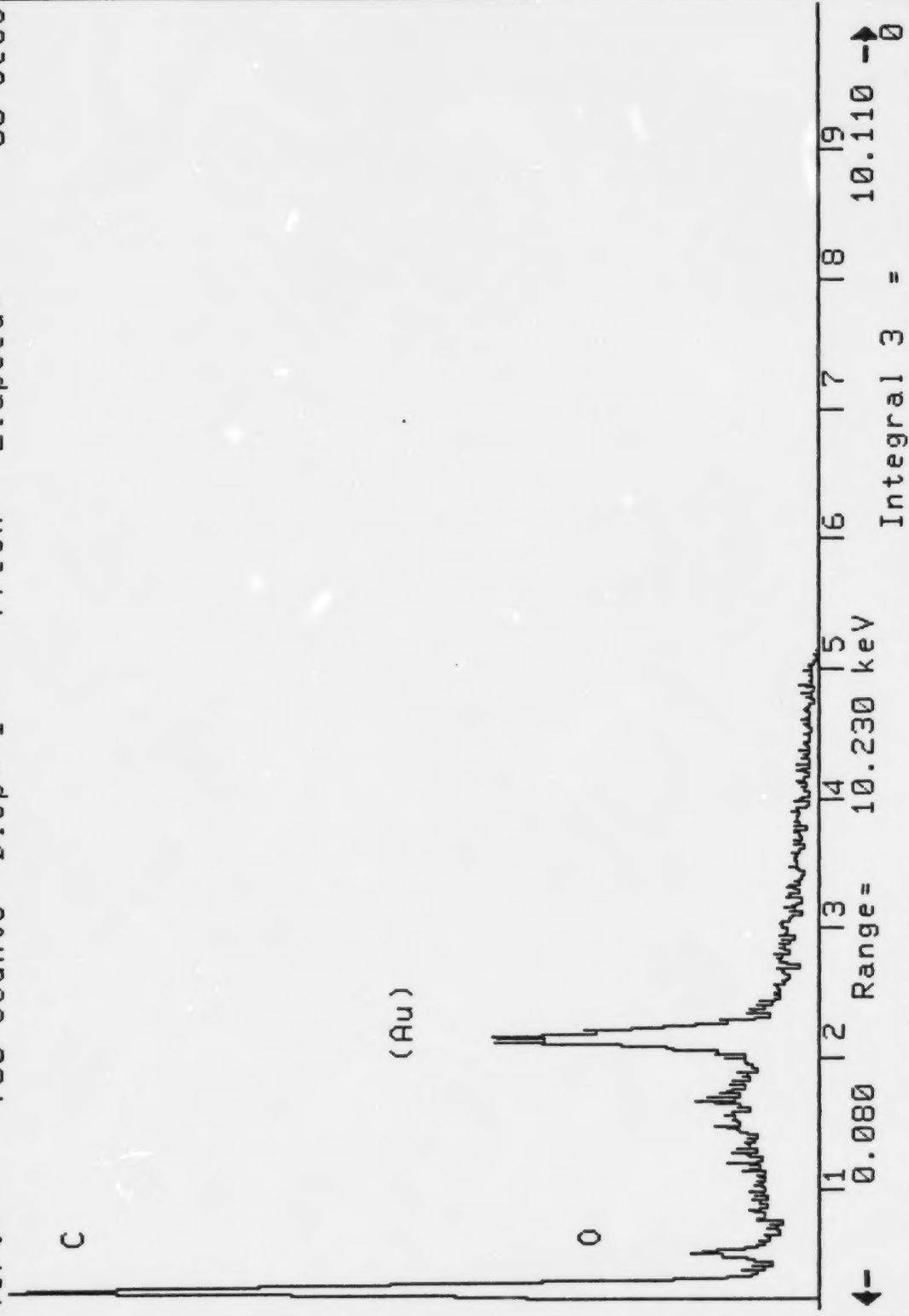
Preset= 60 secs
Elapsed= 60 secs



← 0.000 Range= 10.230 keV Integral 3 = 10.110 → 0

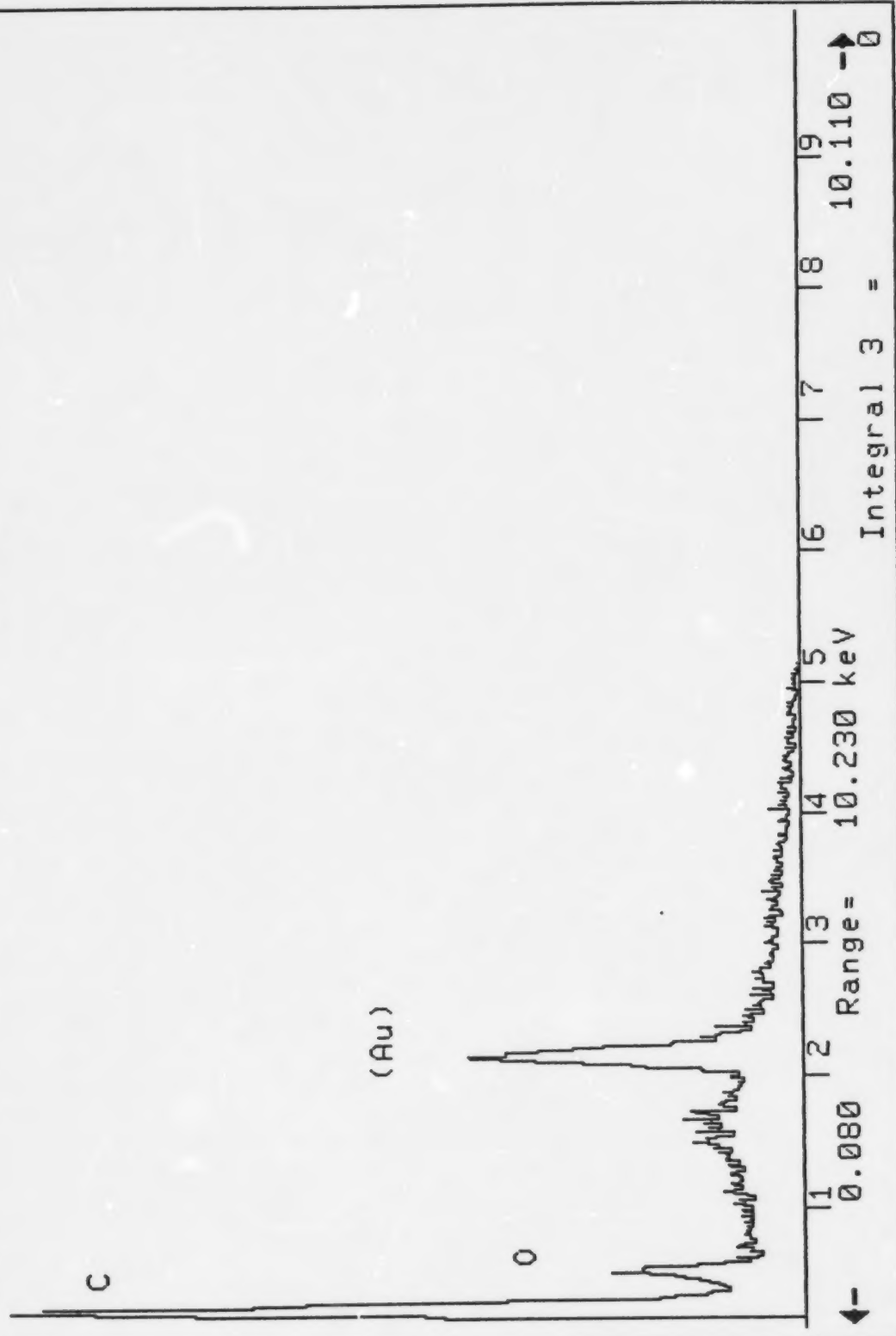
15-Mar-1989 11:56:36

O/C Ratio Analysis-#26 Colly 14 North Preset= 60 secs
Vert= 730 counts Disp= 1 Fresh Elapsed= 60 secs



15-Mar-1989 11:53:50

O/C Ratio Analysis-#26 Colly 14 North Preset= 60 secs
Vert= 909 counts Disp= 1 Oxidized Elapsed= 60 secs

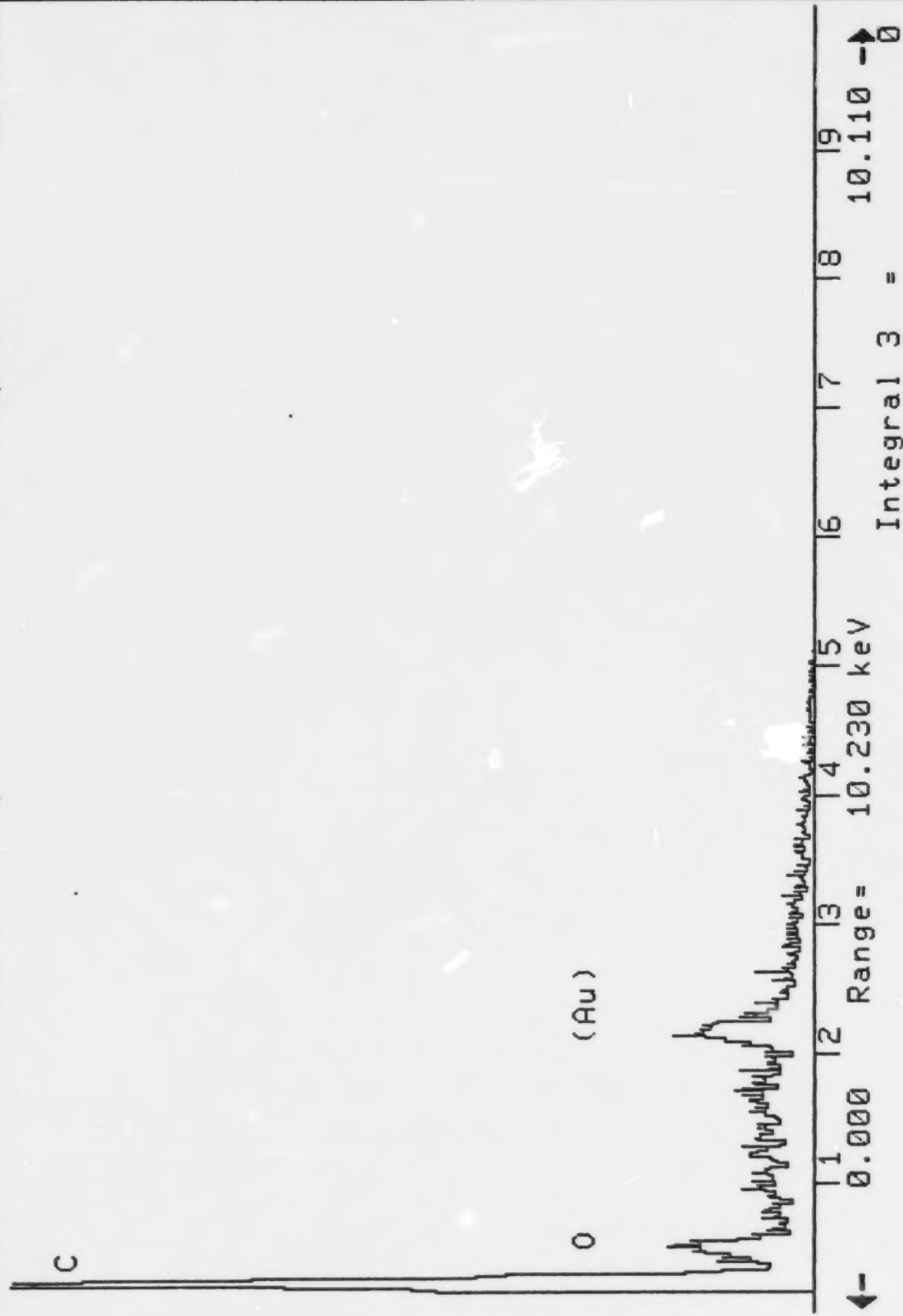


6-Mar-1989 14:08:47

O/C Ratio Analysis - Devco Fresh Coal
Vert= 437 counts Disp= 1

Preset=
Elapsed=

60 secs
60 secs

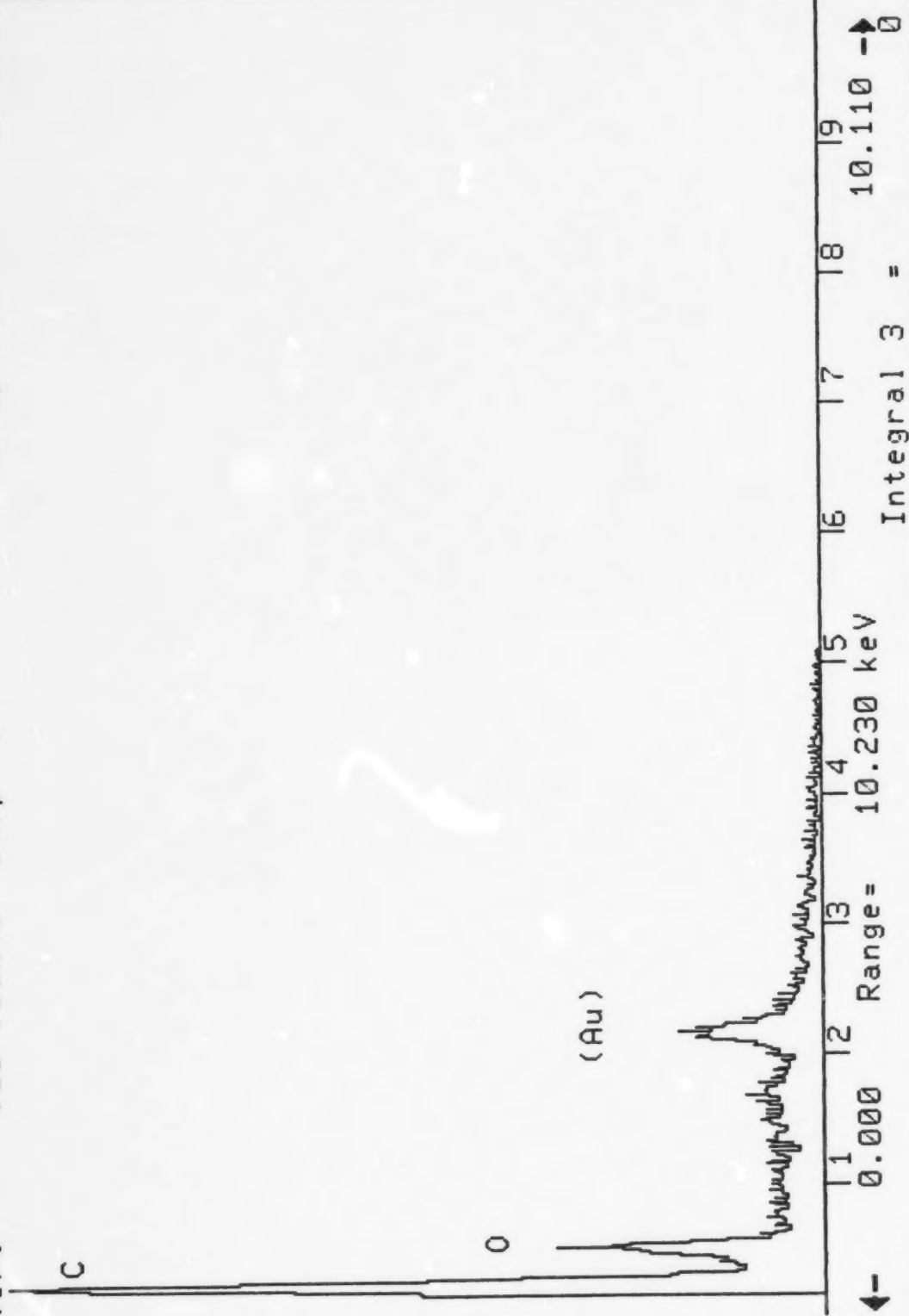


6-Mar-1989 14:11:07

O/C Ratio Analysis - Devco Oxidized
Vert= 735 counts Disp= 1

Preset=
Elapsed=

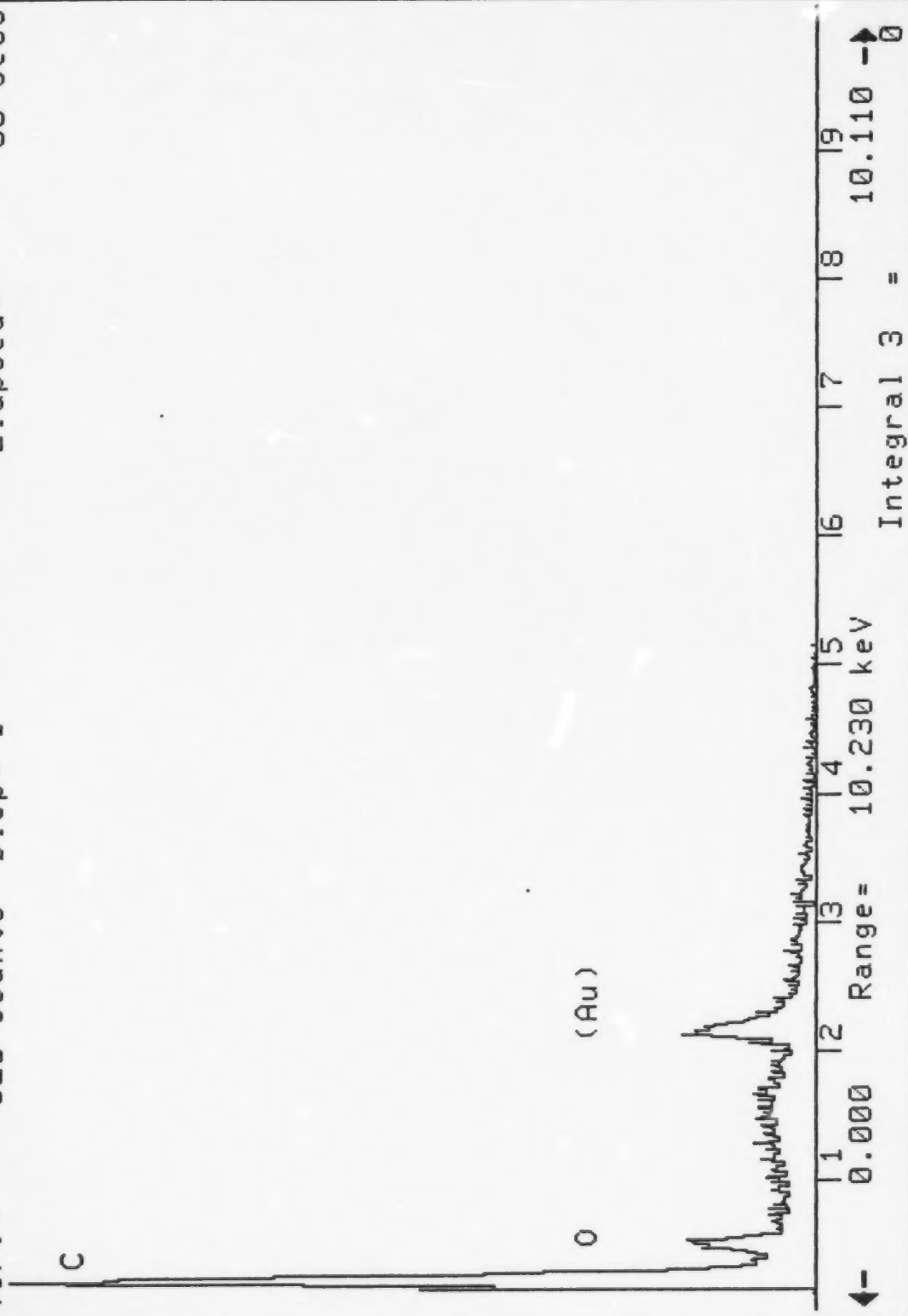
60 secs
60 secs



6-Mar-1989 13:59:08

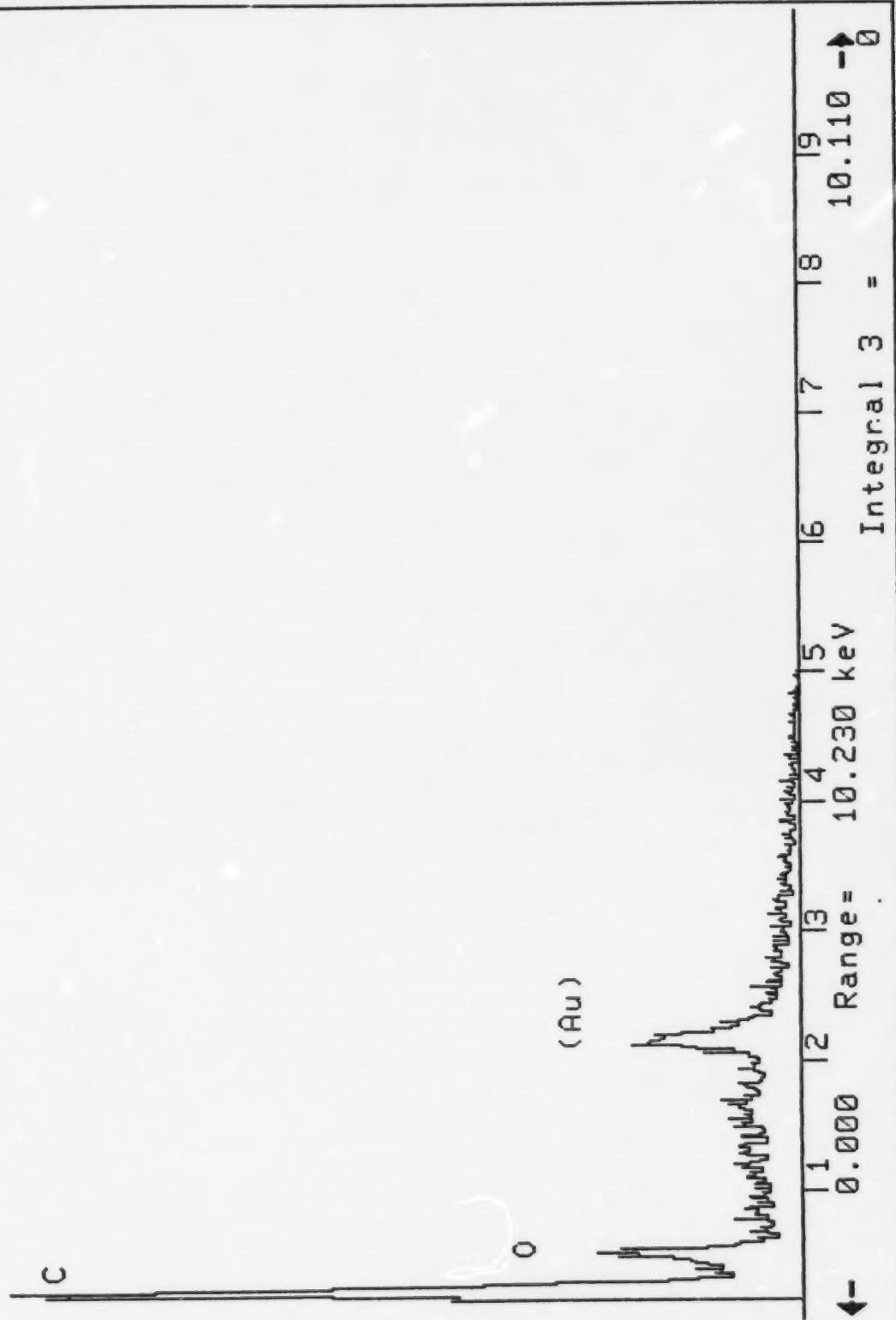
O/C Ratio Analysis - Ligan Raw Fresh CoalPreset=
Vert= 620 counts Disp= 1 Elapsed=

60 secs
60 secs



6-Mar-1989 13:54:32

O/C Ratio Analysis - Ligan Raw Oxidized Preset= 60 secs
Vert= 480 counts Disp= 1 Elapsed= 60 secs

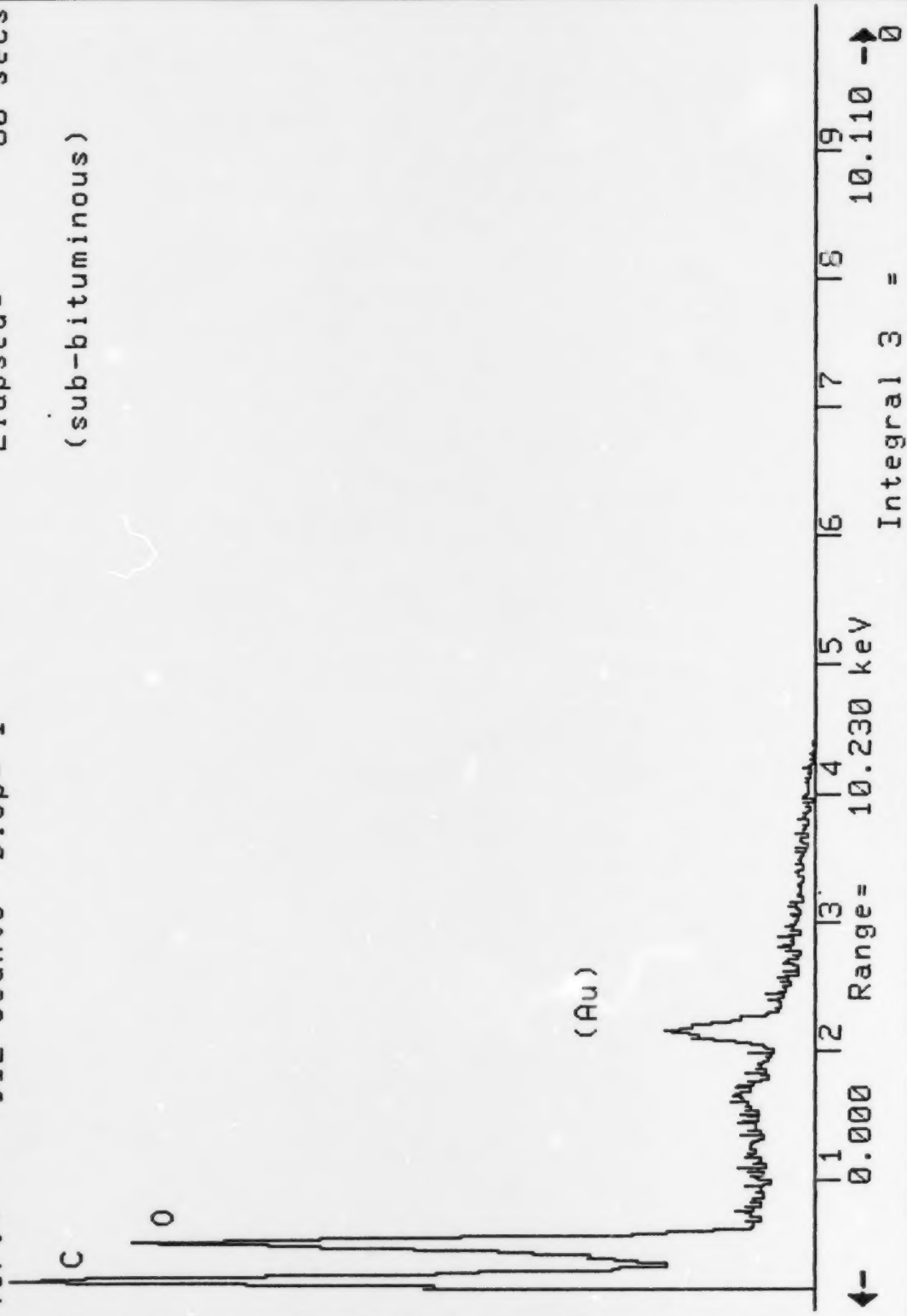


6-Mar-1989 13:45:20

O/C Ratio Analysis - White Wood
Vert= 912 counts Disp= 1

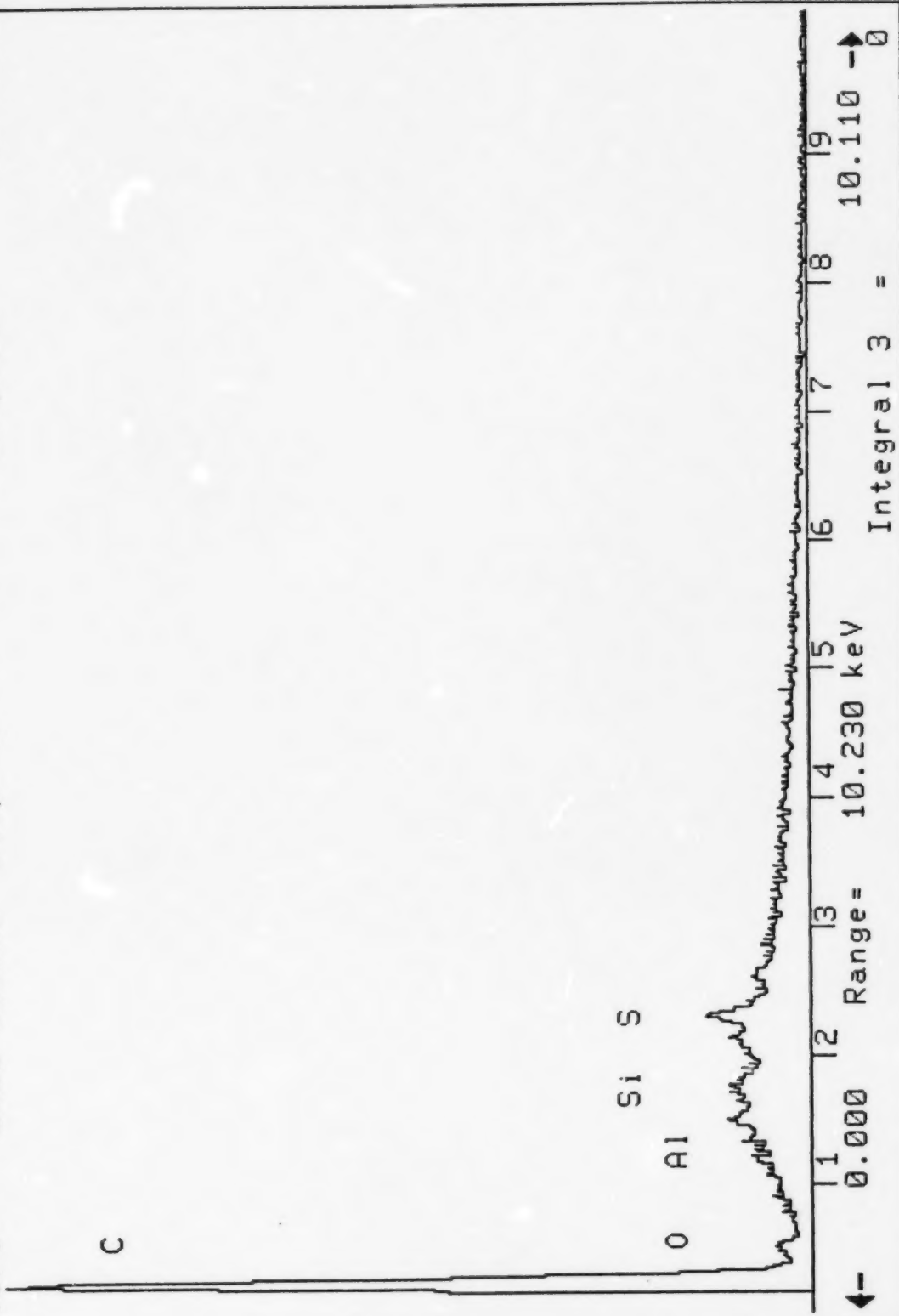
Preset= 60 secs
Elapsed= 60 secs

(sub-bituminous)



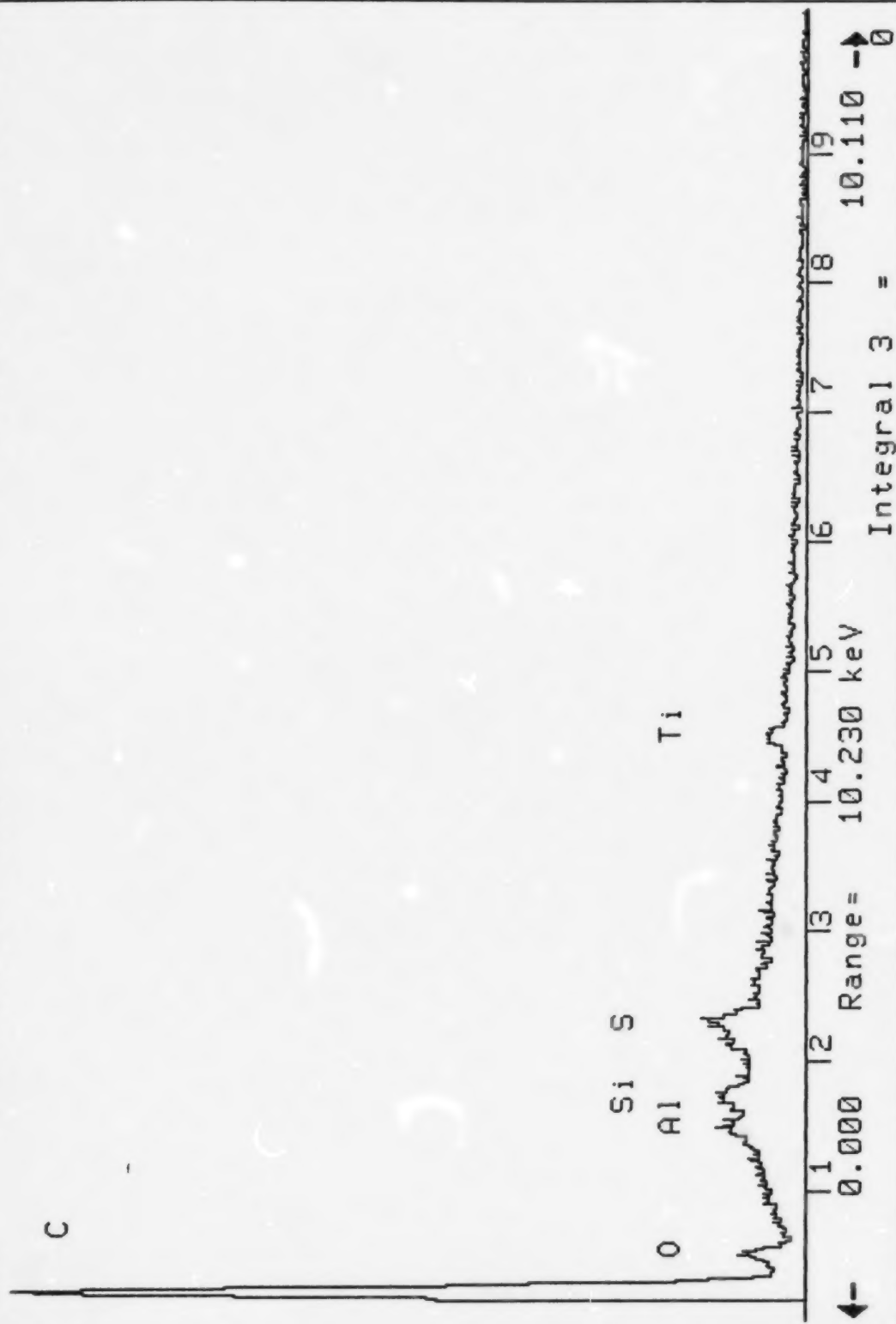
6-Mar-1989 12:55:11

Mineral Analysis - McIntyre Fresh Coal Preset= 100 secs
Vert= 2580 counts Disp= 1 Elapsed= 100 secs



6-Mar-1989 12:58:06

Mineral Analysis - McIntyre Oxidized Coal Preset= 100 secs
Vert= 2869 counts Disp= 1 Elapsed= 100 secs



6-Mar-1989 13:04:54

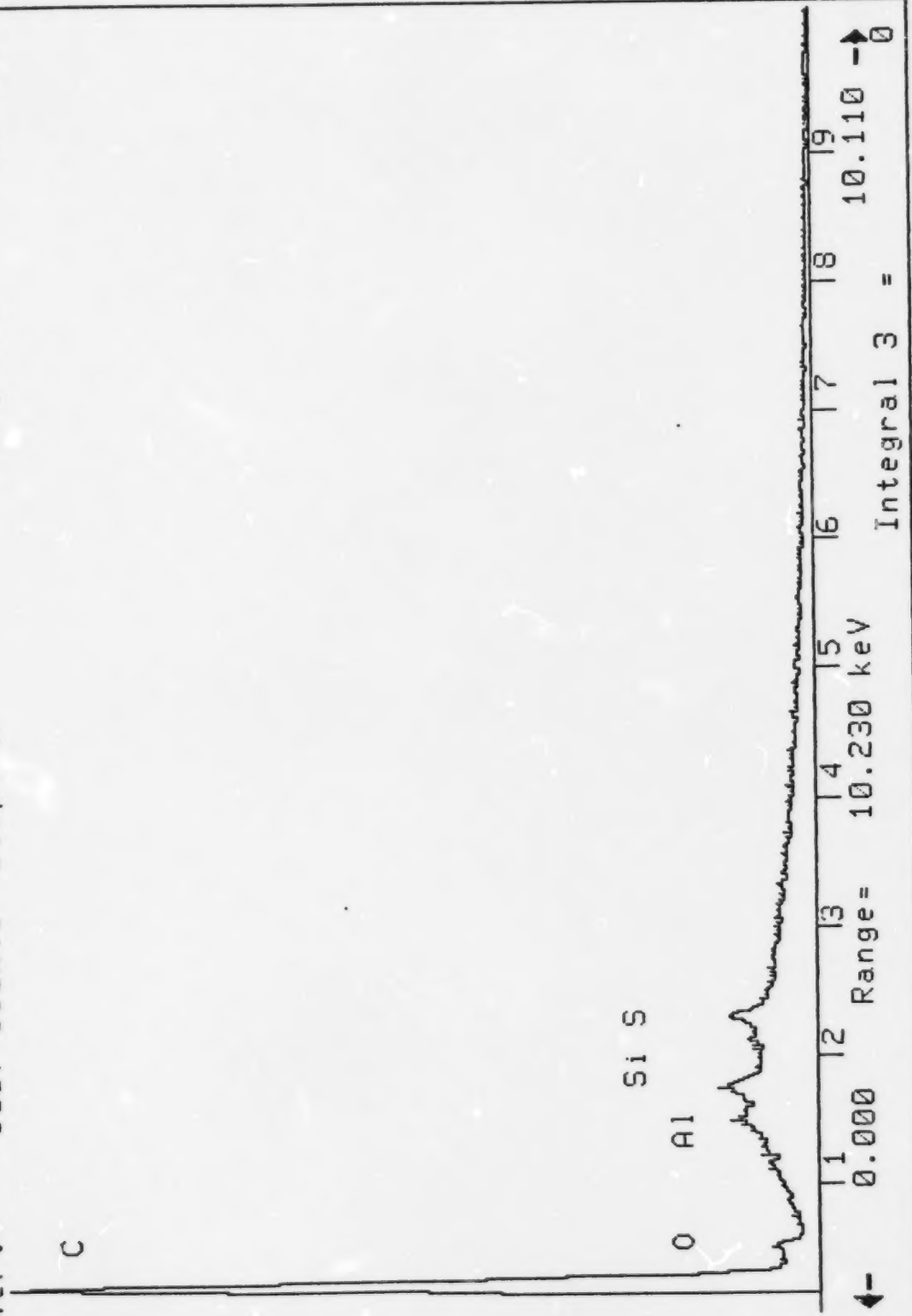
Mineral Analysis - Fording Fresh Coal
Vert = 5607 counts Disp = 1

100 100
sec sec
sec sec

Reset =
Elapsed =

100 sec 100 sec

5607 counts Disp= 1



6-Mar-1989 13:07:23

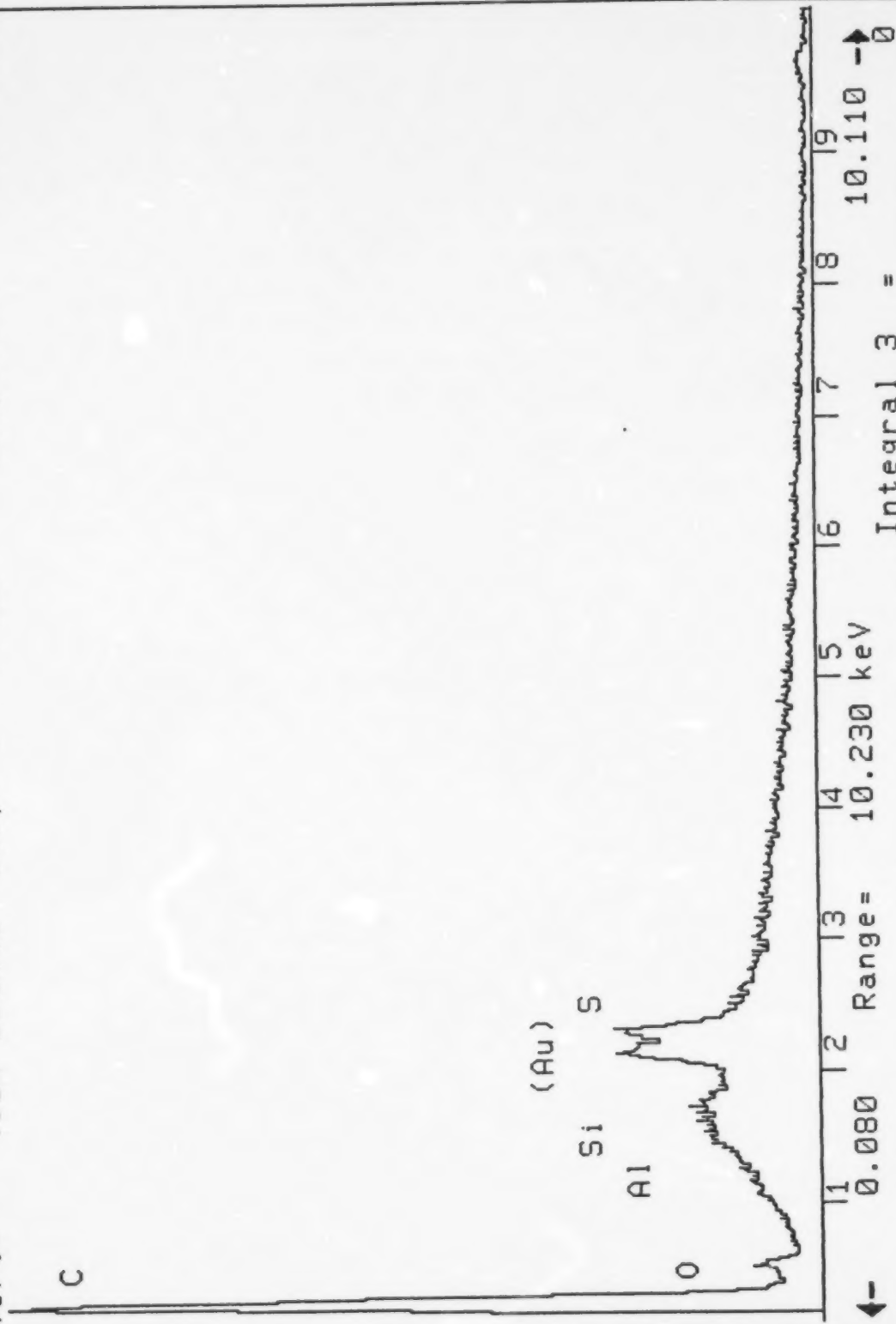
Mineral Analysis - Fording Oxidized Coal Preset= 100 secs
Vert= 4544 counts Disp= 1 Elapsed= 100 secs



15-Mar-1989 12:09:20

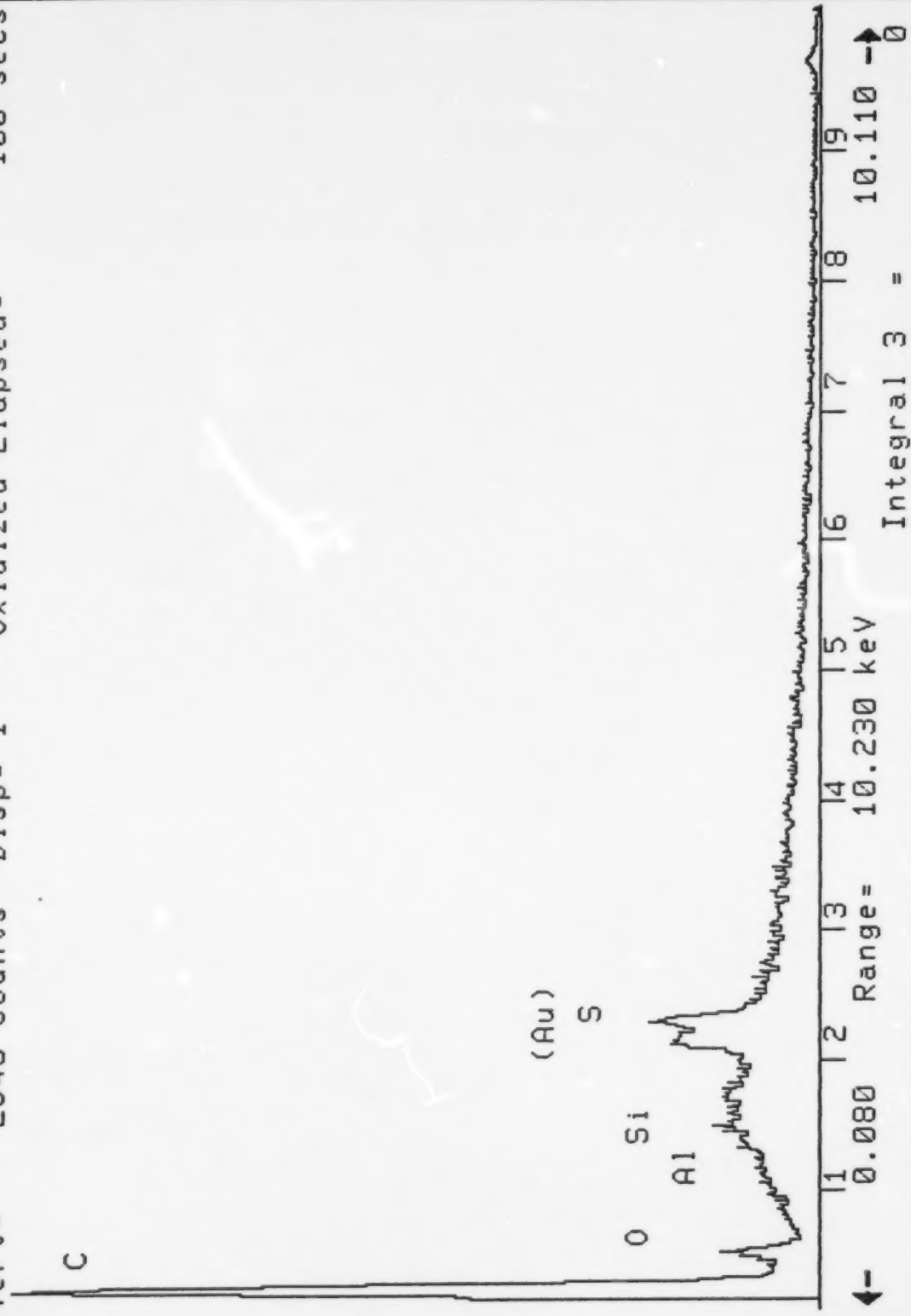
Mineral Analysis-#26· Colly 14 North
Vert= 4134 counts Disp= 1 Fresh

Preset= 100 secs
Elapsed= 100 secs



15-Mar-1989 12:05:52

Mineral Analysis-#26 Colly 14 North Preset= 100 secs
Vert= 2548 counts Disp= 1 Oxidized Elapsed= 100 secs

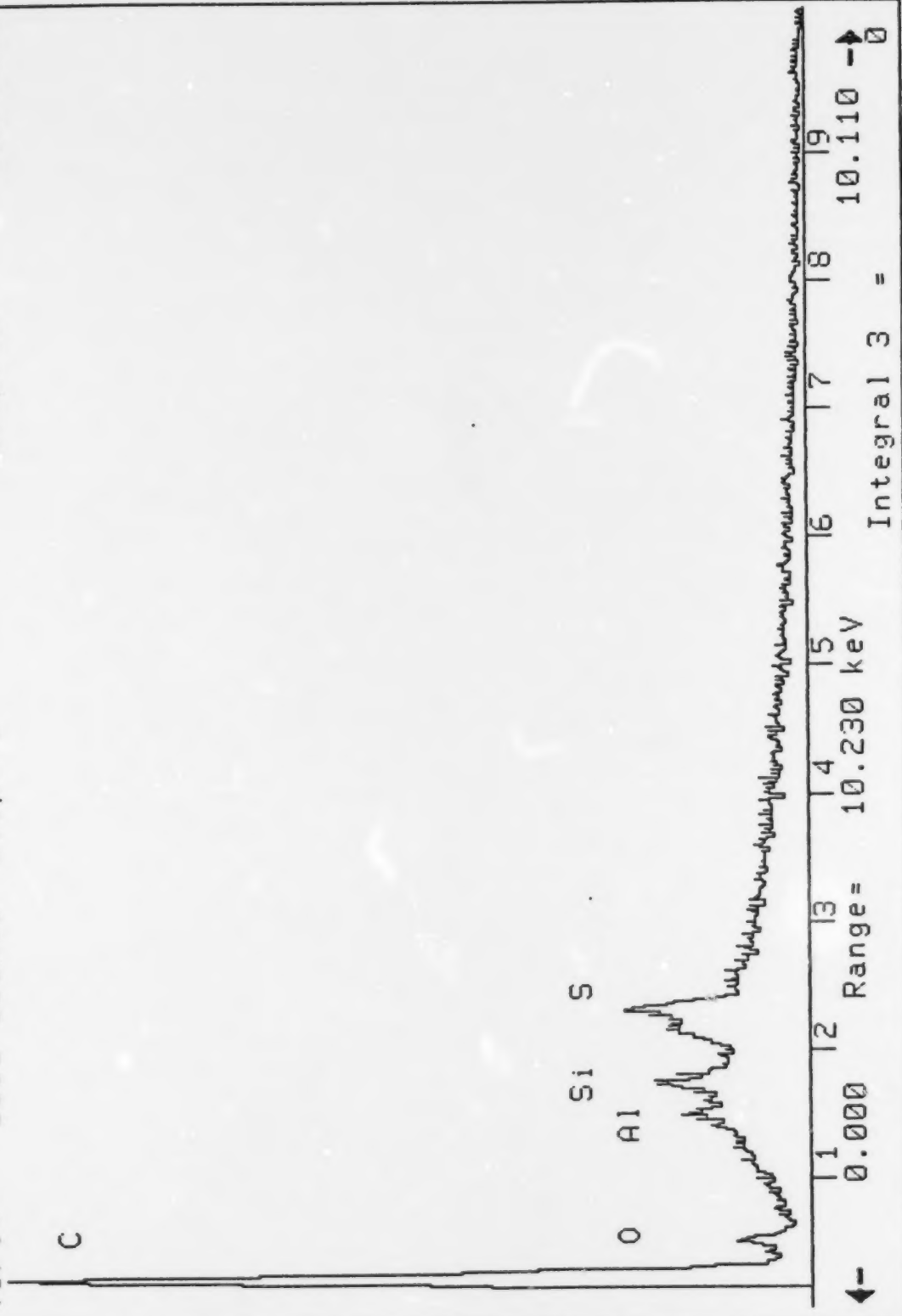


6-Mar-1989 13:14:13

Mineral Analysis - Devco Fresh Coal
Vert= 1553 counts Disp= 1

Preset=
Elapsed=

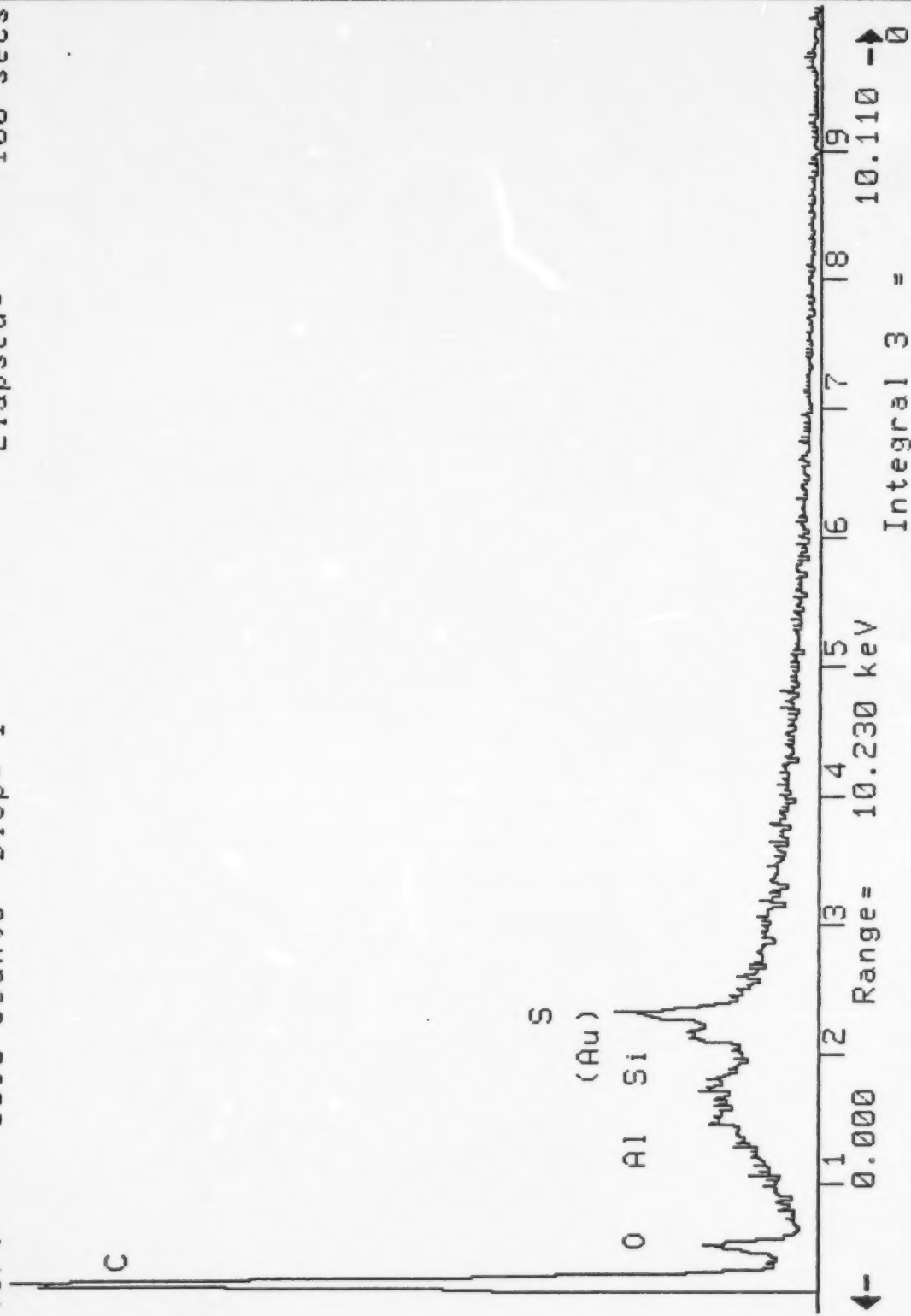
100 secs
100 secs



6-Mar-1989 13:10:20

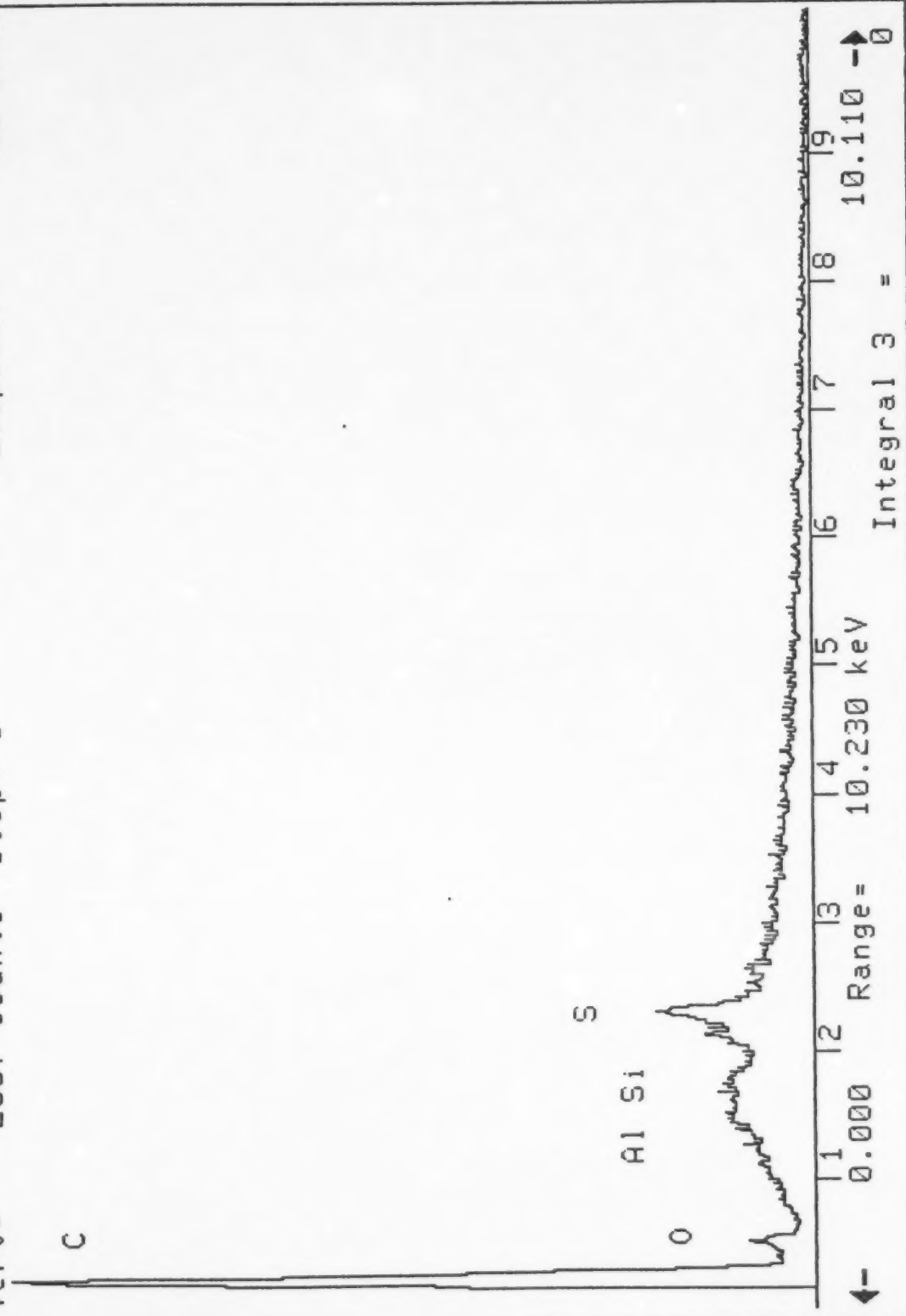
Mineral Analysis - Devco Oxidized Coal
Vert= 1690 counts Disp= 1

Preset= 100 secs
Elapsed= 100 secs



6-Mar-1989 13:16:41

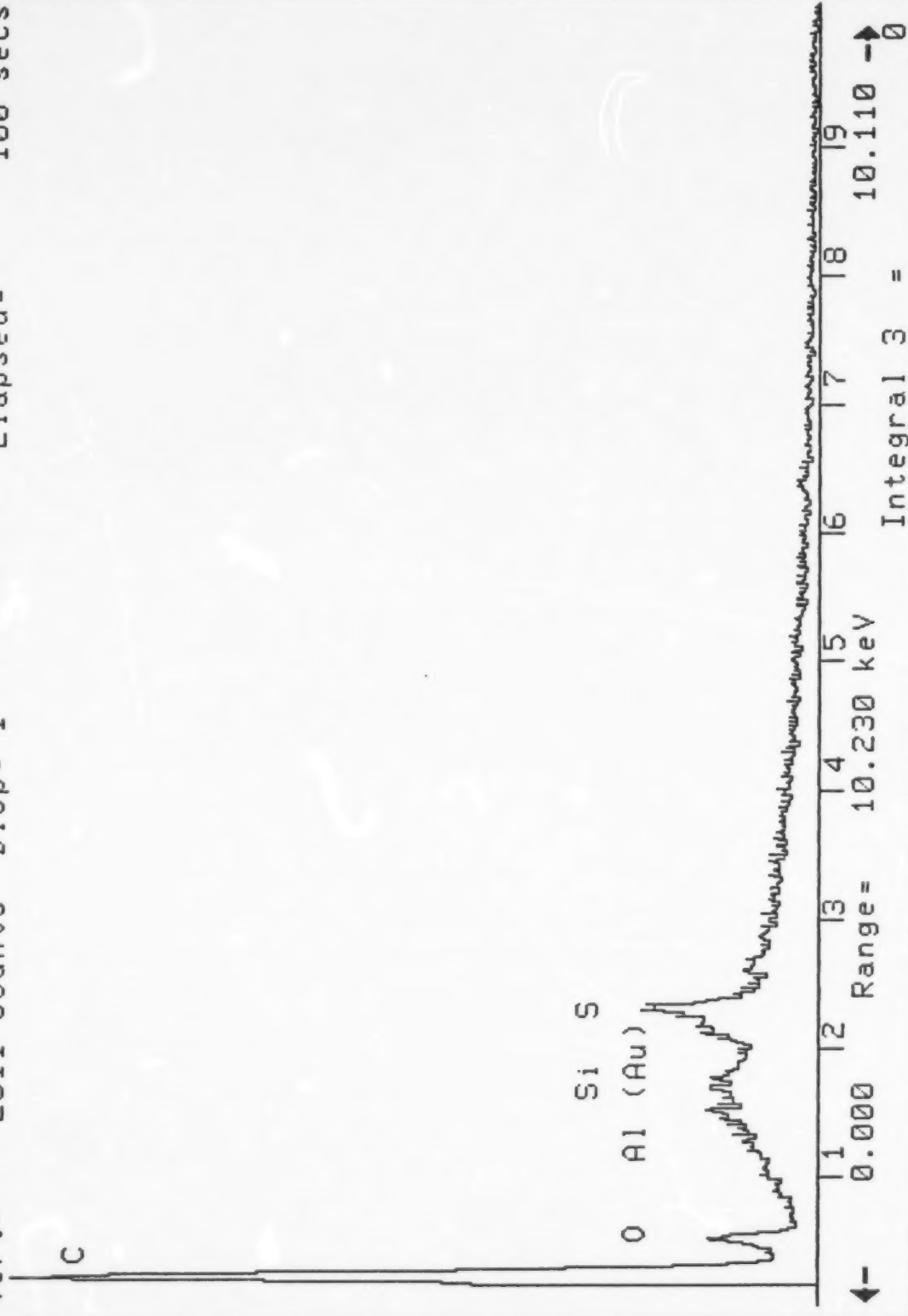
Mineral Analysis - Lingan Raw Fresh Coal Preset= 100 secs
Vert= 2367 counts Disp= 1 Elapsed= 100 secs



6-Mar-1989 13:19:57

Mineral Analysis - Ligan Raw Oxidized
Vert= 2011 counts Disp= 1

Preset= 100 secs
Elapsed= 100 secs

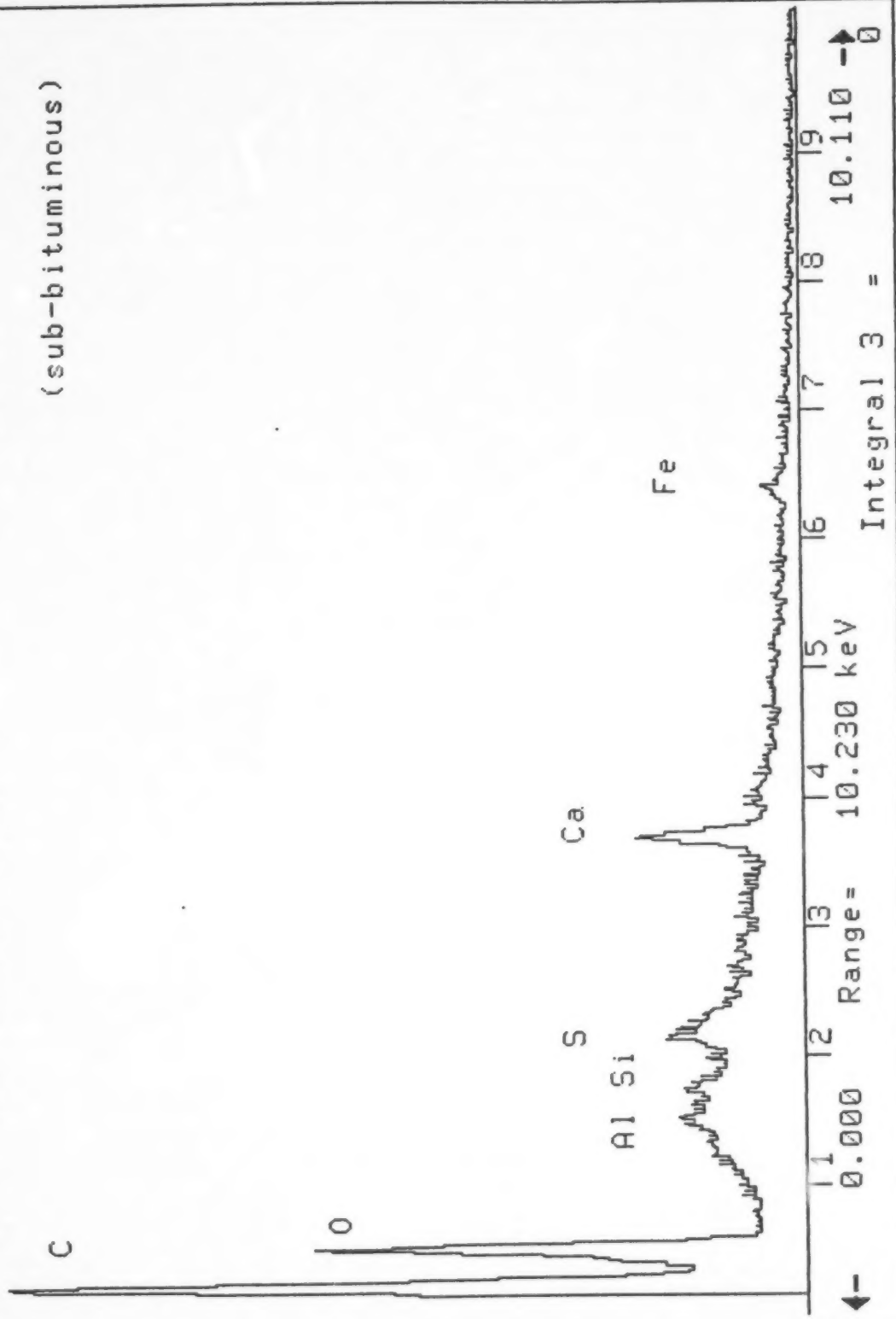


6-Mar-1989 13:02:18

Mineral Analysis - White Wood
Vert= 1962 counts Disp= 1

Preset= 100 secs
Elapsed= 100 secs

(sub-bituminous)



Appendix D: Estimation of Errors

The errors quoted with the values of oxygen content in Table 8 section 3.8 were calculated from the experimentally observed oxygen counts using a simplified version of Currie's Method [8] suggested by R. Packwood [9]. For example, the O/C of 0.200 for the Devco fresh coal sample corresponded to an oxygen peak area intensity of 979 counts and a carbon peak area intensity of 4892 counts. Then:

$$(979)^{\pm} = \pm 32 \text{ counts}$$

$$979 + 32 = 1011 \text{ counts} \quad 1011/4892 = 0.207 \text{ high}$$

$$979 - 32 = 947 \text{ counts} \quad 947/4892 = 0.194 \text{ low}$$

Calculating the oxygen content from these high and low O/C ratios yields values of 10.2% O high and 9.5% O low. Subtracting these two values gives an error range of 0.7% and an error of $\pm 0.35\%$.

Appendix E: QRL Optical Photographs



FIGURE 7 Optical 100X No Gold Coating



FIGURE 8 Optical 100X Gold Coating

Appendix F: ResumesRay F. Haythornthwaite

Graduated from Nottingham University in UK in 1960 with a Chemistry degree after working for a period in a coal gasification plant. He was employed in semiconductor production and development before becoming a senior reliability engineer with Philips. After emigrating to Canada in 1970, he worked on reliability aspects of the Canadian Space Programs for 10 years specializing in semiconductor device and material analysis. During this time he obtained MEng and PhD degrees part time from Carleton University in semiconductor instabilities and the use of the SEM to study properties of GaAs devices. He joined QRL Analysis Corporation in 1980 and has been president since 1985. At QRL he has specialized in aerospace electronics reliability, metallurgical failure analyses and materials analysis.

Chantal M. Hemens

Received BSc with honour's in Chemistry, in 1986, from St. Mary's University, Halifax, N. S. She graduated from Queen's University in Kingston, Ont. with her Master of Science in Analytical Chemistry in 1988. Chantal joined QRL Analysis Corporation in July 1988 where she specializes in material analysis and developing new analytical techniques employing electron microprobe microanalysis. Chantal has eight publications in areas of chemical synthesis, chemical characterization and emphasis on method development of specific chemical procedures.